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STRUCTURE AND REACTIVITY OF ADSORBED OXIDES OF SULFUR

Jack H. Lunsford

Texas A and M University

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ABSTRACT

The purpose of the research reported here was to determine the structure and reactivity of adsorbed oxides of sulfur and other small sulfur-containing molecules. The molecules that were studied include the anion radicals of sulfur dioxide, sulfur trioxide, a triatomic sulfur species and carbonyl sulfide. Diamagnetic sulfite and sulfate ions, as well as covalently bonded oxides of sulfur, were also studied. The adsorbent was a high surface area magnesium oxide powder. Electron paramagnetic resonance and infrared spectroscopy were used to characterize the surface species.

The results show that electronegative molecules such as sulfur dioxide adsorb either by an electron transfer from the solid, forming a negative radical ion, or by reacting with the oxide ions of the lattice. At room temperature the adsorbed sulfur dioxide anion radical may be oxidized with molecular oxygen to the sulfur trioxide anion radical; whereas, at elevated temperatures the sulfite ions may be oxidized. In contrast, the anion radical of carbonyl sulfide is very unstable and dissociates, presumably to elemental sulfur and carbon monoxide, at low temperatures. Elemental sulfur reacts with partially hydroxylated magnesium oxide, forming the

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triatomic negative ion, hydrogen sulfide, and other unidentified products.

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SECTION I

CONCLUSIONS

Results from this research have demonstrated that SO_2 reacts with the surface of magnesium oxide, forming a number of different surface ions. If the surface has a reducing character, the thermally stable SO_2^- ion is formed. In high concentrations on the surface this ion reacts with molecular oxygen to produce the SO_3^- ion, which may be an intermediate in the catalytic oxidation of SO_2 to SO_3 .

Exposure of magnesium oxide to SO_2 also results in the formation of two types of SO_3^{2-} ions which are hydrogen-bonded to surface hydroxyl groups. These two species correspond to two different active sites on the surface of MgO . The number of sites, as reflected by the intensity ratio of the bands of the two SO_3^{2-} species, depends on the pretreatment of the MgO catalyst. At temperatures above 500°C , SO_3^{2-} is unstable and decomposes. As a consequence, after degassing at 800°C under vacuum, residual bands are present which are attributed to a SO_4^{2-} surface species. When the adsorbed SO_3^{2-} ion is heated in O_2 , a complex infrared spectrum is observed which corresponds to a mixture of bidentate and chelate sulfato complexes along with strongly bonded SO_3 .

Other radical anions such as COS^- and CS_2^- are formed upon reacting the corresponding neutral molecule with a reducing magnesium oxide surface. These surface ions are thermally unstable at room temperature, and the COS^- ion dissociates, yielding CO and presumably elemental sulfur.

Partially hydroxylated magnesium oxide reacts with elemental sulfur to form polymeric radicals at temperatures around 200°C and a triatomic sulfur ion, S_3^- , at 400°C . The latter reaction is accompanied by the production of H_2S , which desorbs from the surface. The S_3^- ion reacts with molecular oxygen at room temperature, yielding an unidentified diamagnetic product.

It is clear from these studies that sulfur and its oxides undergo numerous chemical changes on the surface of magnesium oxide, which may be taken as a typical basic surface. The chemistry of these systems may be conveniently studied by epr and ir techniques. Although these results have been obtained under ideal conditions which do not duplicate the atmosphere, the spectra of potentially important species have been identified, and the work may now be extended to more realistic conditions.

SECTION II

RECOMMENDATIONS

A comprehensive understanding of the effects of aerosols on animal and human physiology will require detailed information on the structure and reactivity of surface species. The concentration of sulfur oxides is usually reported simply as "sulfates"; however, the results of this work and similar studies clearly demonstrate that many different sulfur oxides may be stabilized on a model surface. The types of sulfur oxides which exist on aerosols in a real atmosphere have yet to be conclusively identified, although one may be reasonably sure that other forms of sulfur than as sulfate ions will be found.

It is recommended, therefore, that the work reported here be extended in two directions. First, the work on pure metal oxides should be continued, but the adsorbents should more closely correspond to the composition of aerosols in the earth's atmosphere and any irradiation of the sample should simulate the solar spectrum. Second, the project should be expanded to include studies of collected atmospheric aerosols which have varying sulfur content. The samples should be studied as received and after exposure in the laboratory to atmospheres containing different levels of SO_2 . Results from such studies should elucidate some of the complex chemistry which must be taking place at the surface of the aerosol samples.

SECTION III

INTRODUCTION

GENERAL

The overall objective of the research was to determine the structure and reactivity of adsorbed oxides of sulfur and other small sulfur-containing molecules. Magnesium oxide was used as a representative metal oxide surface. The surface species were identified by electron paramagnetic resonance (epr) and infrared (ir) spectroscopy. The scope of the study included paramagnetic ions SO_2^- , SO_3^- , S_3^- and COS^- as well as the diamagnetic ions SO_3^- and SO_4^- . Other covalently bonded oxides of sulfur were also detected.

SO_2^- AND SO_3^- ON MAGNESIUM OXIDE

Sulfur dioxide is a very electronegative molecule which readily forms the SO_2^- ion upon adsorption, provided electrons at a sufficient potential are available at the surface. Mashchenko, Pariiskii, and Kazanskii¹ reported the formation of SO_2^- as well as diamagnetic species, on partially reduced TiO_2 by adsorption of SO_2 . These authors also presented evidence that the reaction of SO_2^- with O_2 on the TiO_2 surface leads to O_2^- and vice versa through intermediate surface sulfates, but they strongly emphasized that the reaction of SO_2^- with O_2 leads mainly to diamagnetic species.

It was our intention to extend these studies to activated MgO where it is possible to trap electrons on the surface of

a suitably prepared sample.² Upon adsorption of SO_2 the electron is transferred to the sorbed SO_2 molecule to form SO_2^- . The characteristic molecular parameters of the SO_2^- on the surface of MgO have been determined by evaluating the g tensor and the ^{33}S and ^{17}O hyperfine tensors. These values are compared with those obtained from SO_2^- trapped in solid matrices. Also, the thermal stability of SO_2^- has been investigated, as well as the effects of different pretreatments of the MgO catalyst. The results are interpreted in terms of the molecular orbital of the odd electron in SO_2^- and the nature of the adsorption sites on the MgO surface.

Reactions involving the SO_2^- ion on surfaces have been studied in an effort to determine the importance of this species in the catalytic oxidation and reduction of SO_2 . It will be subsequently shown that under proper conditions the SO_2^- ion reacts with molecular oxygen to form the adsorbed SO_3^- ion. The epr spectrum of SO_3^- has been well characterized by Chantry and coworkers.³ In their studies the ion was formed upon γ -irradiation of a number of salts such as sodium dithionate, which has an unusually long S-S bond. From the ^{33}S hyperfine structure it was possible to compare SO_3^- with the isoelectronic ions PO_3^{2-} and ClO_3^- . More recently Lind and Kewley⁴ also observed the spectrum of SO_3^- upon γ -irradiation of taurine. This natural amino acid in its zwitterion form ($\text{H}_3\text{N}^+-\text{CH}_2-\text{CH}_2\text{SO}_3^-$) undergoes homolysis of the C-S bond, thus generating the SO_3^- ion.

COS^- AND CS_2^- ON MAGNESIUM OXIDE

Like SO_2 , COS and CS_2 are able to accept trapped electrons from the magnesium oxide surface, forming the respective radical

anions. Since COS is an intermediate in the catalytic reduction of SO_2 by CO, information regarding the stability of COS^- on surfaces was of interest. In a recent mass spectrometric study MacNeil and Thynne⁵ observed only the decomposition products for COS at electron energies less than 1 eV, but no COS^- was detected; hence the ion must be unstable in the gas phase. On the other hand CO_2^- is stable on the surface of MgO ⁶. Although the molecule ions CO_2^- and CS_2^- have been studied in detail by epr spectroscopy, the spectrum of the isoelectron COS^- ion had not previously been reported.

S_3^- ON MAGNESIUM OXIDE

Elemental sulfur and sulfur ions play an important role in the behavior of catalysts for desulfurization reactions and the reduction of SO_2 over metal oxides. The state of the sulfur on the surface has been studied, mainly by epr spectroscopy; but the spectra are usually lacking in hyperfine structure and it is difficult to make a positive identification of the surface radicals. The sulfur ions S^- , S_2^- and S_3^- have been identified in single crystals on the basis of their g tensors and hyperfine structure. The oxygen ions O^- , O_2^- and O_3^- are easily formed on a magnesium oxide surface, and it seems reasonable that the analogous sulfur ions could be stabilized on the surface. However, the lower vapor pressure of sulfur and a tendency to produce polynuclear molecules make it difficult to produce S^- and S_2^- on MgO . Evidence is presented here for the formation of S_3^- upon reacting elemental sulfur with a partially hydroxylated magnesium oxide surface. The sulfur-33 hyperfine splitting was used to identify the molecule and to establish its structure.

SULFITE AND SULFATE IONS ON MAGNESIUM OXIDE

Sulfur dioxide also forms several stable diamagnetic species upon adsorption at metal and metal oxide surfaces. On porous silica glass⁷ SO_2 displaces the 3750 cm^{-1} band of the free hydroxyl groups to a lower wave number by 115 cm^{-1} . On Fe and Ni surface SO_2 adsorbs chemically to form a SO_4 surface species, which is believed to be an intermediate in the catalytic oxidation of SO_2 to SO_3 ⁸. Such a strong chemical change is not always observed. Habgood and coworkers⁹ studied the adsorption of H_2S and SO_2 on γ -alumina, NaOH-doped γ -alumina, NaY and HY zeolites. Except for NaY, where no OH groups were present in measureable amounts, SO_2 adsorbed on these samples through strong hydrogen bonding. After heating up to 400° under dynamic vacuum the adsorbed SO_2 molecules on γ -alumina and on NaOH-doped γ -alumina transformed to a chemisorbed species. A sulfate-like structure involving two lattice oxygens and the adsorbed SO_2 molecule was suggested as an explanation. However, the Si-O and Al-O adsorption bands in the $700\text{--}1200\text{ cm}^{-1}$ region obscure the S-O vibrations of this SO_4 species and no unambiguous proof could be advanced by these authors.

The infrared spectrum of SO_2 on CaO and MgO has recently been studied by Low and coworkers^{10,11}. They observed that the main interaction of SO_2 with degassed CaO is irreversible and leads to the formation of a surface sulfite; however, reversible chemisorption occurs at high degrees of surface coverage. On heating the sample under vacuum at 550°C a new spectrum attributed to a surface sulfite and polymerization are thought to occur. Heating in oxygen resulted in a spectrum

which resembles that of bulk CaSO_4 . On MgO Low proposed that the adsorption of SO_2 resulted in the formation of monodentate- and bidentate-like surface sulfites which could only be removed by degassing at high temperatures. A reversible chemisorption occurred at high degrees of surface coverage. SO_2 was then physically adsorbed on top of the more tightly bound species. Heating in oxygen converted the adsorbed material to species resembling bulk MgSO_4 .

SECTION IV

MATERIALS AND METHODS

The MgO used in these experiments was a reagent grade powder supplied by Mallinckrodt Chemical Works. The powder was boiled in distilled water for 2-3 hr, during which time it was converted mainly to $\text{Mg}(\text{OH})_2$. The slurry was dried at 100°C until a paste was obtained. For the epr experiments the $\text{MgO}/\text{Mg}(\text{OH})_2$ paste was extruded into pellets, approximately 1 mm in diameter, with a hypodermic syringe and then dried at 100°C . For the ir experiments a small amount of the paste was spread over a 2 x 1 cm platinum grid. The film obtained in this manner was fitted in the quartz side-arm of the infrared cell depicted in Figure 1. One sample was studied without the platinum grid in order to demonstrate that the platinum did not influence the reactions. Because of the platinum grid it is difficult to give an accurate sample density; however, a value of $20 \text{ mg}/\text{cm}^2$ of MgO may be used for comparison purposes.

Pretreatment of the sample varied from one type of experiment to another. In the formation of SO_2^- ions, the $\text{MgO}/\text{Mg}(\text{OH})_2$ was heated under vacuum to 500° or 800°C for 5 to 7 hr, which converted the $\text{Mg}(\text{OH})_2$ to a high surface area MgO. The activated MgO was placed in contact with very pure H_2 and the sample was uv-irradiated with a low-

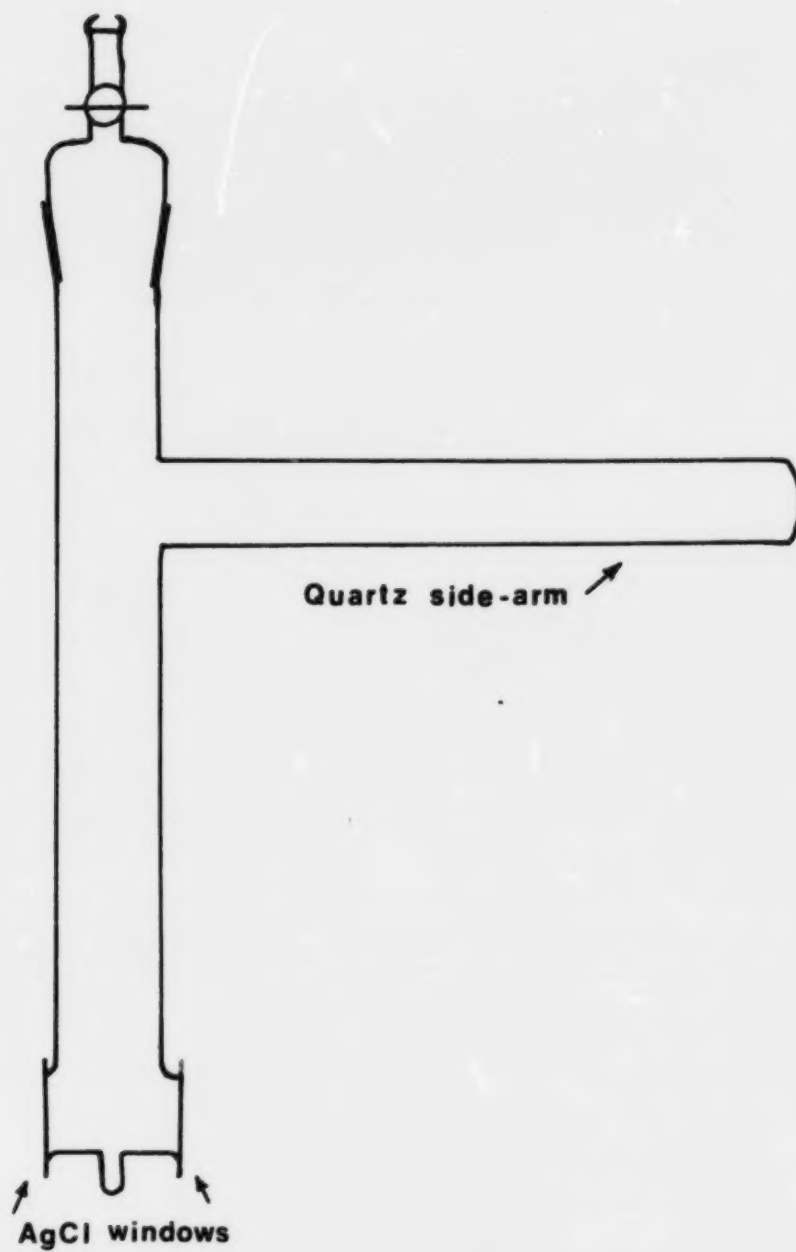


Figure 1. Infrared cell with quartz side-arm and AgCl windows.

pressure mercury vapor lamp ($\lambda = 2537\text{\AA}$). The MgO became blue due to electrons trapped at surface centers (S-centers). Ultraviolet irradiation at liquid N_2 temperatures produced more S-centers in a much shorter period of time than at room temperature. Alternately, the uv irradiation was performed after the SO_2 adsorption. In this case no hydrogen was used.

For the formation of SO_3^- , the MgO/Mg(OH)_2 was degassed for 2 hr at 350°C and for 1 hr at either 450 or 850°C . The S centers, formed in the same manner as before, were subsequently allowed to react with purified N_2O or SO_2 producing O^- or SO_2^- on the surface. Alternately, the activated MgO was irradiated at room temperature in the presence of N_2O which yielded adsorbed O_3^- , as well as excess O_2 and N_2 .

The molecule ions CO_2^- and COS^- were formed by first producing S centers on activated MgO and then adsorbing either COS or CO_2 at -135°C or -78°C . The samples were rapidly cooled to -196°C and maintained at that temperature.

For the formation of S_3^- the MgO/Mg(OH)_2 was degassed under vacuum at 300°C for 2 hr and 450°C for 1 hr. Elemental sulfur was kept in a 4 mm quartz sidearm of the reactor. After the MgO had been degassed, it was tapped into the quartz sidearm on top of the sulfur, and the sidearm was heated, usually to 400°C . Generally the sample had to be heated 16 hr at 400°C for the maximum S_3^- spectrum to appear.

Typical pretreatments for the ir studies consisted in evacuating the sample in the sidearm of the ir cell to 1×10^{-5} Torr and subsequently heating it to 300 , 500 or 800°C for 3-7 hr. After cooling the film was allowed to glide

between the two AgCl windows. Magnesium oxide is not transparent below 700 cm^{-1} . Spectra were taken at 25°C under vacuum in the regions $700\text{--}1700\text{ cm}^{-1}$ and $3100\text{--}3800\text{ cm}^{-1}$ after each pretreatment. About 3 Torr of pure SO_2 was allowed into the cell. Spectra were taken in the same wavenumber regions soon after the SO_2 introduction and at several stages of the subsequent desorption-reaction process. In this latter procedure the sample was heated under vacuum up to 800°C in intervals of 200°C . The sample was equilibrated for 2 hr at each 200° interval, cooled, and the spectrum was recorded.

The reactivity of the adsorbed species towards O_2 was also investigated. For this purpose SO_2 was adsorbed and subsequently degassed at 500°C for 2 hr under vacuum. The spectrum was taken from $700\text{--}1500\text{ cm}^{-1}$ and $3100\text{--}3800\text{ cm}^{-1}$ at room temperature. This was followed by the introduction of about 150 Torr O_2 . The sample was then heated for 2 hr in the O_2 atmosphere at 200, 400, 600 and 800°C . After each step the spectra were recorded in the same wavenumber ranges at room temperature without previous evacuation of the excess O_2 .

The anhydrous SO_2 used in these experiments was obtained from a commercial source, and was purified several times by the freeze-pump technique prior to use. Sulfur enriched with 25 and 44% ^{33}S and oxygen enriched with 47% ^{17}O were used to produce enriched $^{33}\text{SO}_2$ and $\text{S}^{16}\text{O}^{17}\text{O}$, respectively. Suitable amounts of oxygen and sulfur were allowed to react at 450°C for 1-4 hr.

The epr spectra were obtained with a Varian Model V-4500 or E-6S spectrometer. Spectra were recorded at both X-band and Q-band microwave frequencies. The g tensors were evaluated

by using a phosphorus-doped silicon standard which had a g value of 1.9987.

All infrared spectra were recorded with a Beckman IR-12 spectrophotometer in the absorbance mode. The estimated error in the assignment of wave numbers is $\pm 5 \text{ cm}^{-1}$ for sharp bands and $\pm 10 \text{ cm}^{-1}$ for broad bands.

SECTION V

RESULTS

SO_2^- ON MAGNESIUM OXIDE

When SO_2 was allowed to absorb on previously uv-irradiated MgO , which had been degassed at 500° , the spectra of Figure 2 were obtained. This figure shows a decrease in intensity of the S-center with a simultaneous increase in the SO_2^- spectrum. It is also apparent that two SO_2^- species are formed on the surface of MgO . The species with the highest g values, SO_2^- (A), appeared first followed by the SO_2^- with slightly lower g values, SO_2^- (B). With increased SO_2 adsorption the SO_2^- (B) becomes the predominant species. When all the sites are saturated, the ratio SO_2^- (B): SO_2^- (A) approximately equals two.

When MgO was pretreated at 800° , qualitatively the same results were obtained. The difference being the final ratio of SO_2^- (B): SO_2^- (A): as shown in Figure 3 the ratio for this case is less than unity if one considers the doubly integrated signal.

A sample, previously saturated with SO_2^- , undergoes exactly the reverse behavior when heated under vacuum. Although both SO_2^- species were stable under a dynamic vacuum of 10^{-5} Torr at room temperature, the SO_2^- (B) species disappeared far more rapidly than the SO_2^- (A) species with increasing temperature. Essentially no SO_2^- (B) is apparent following the treatment at

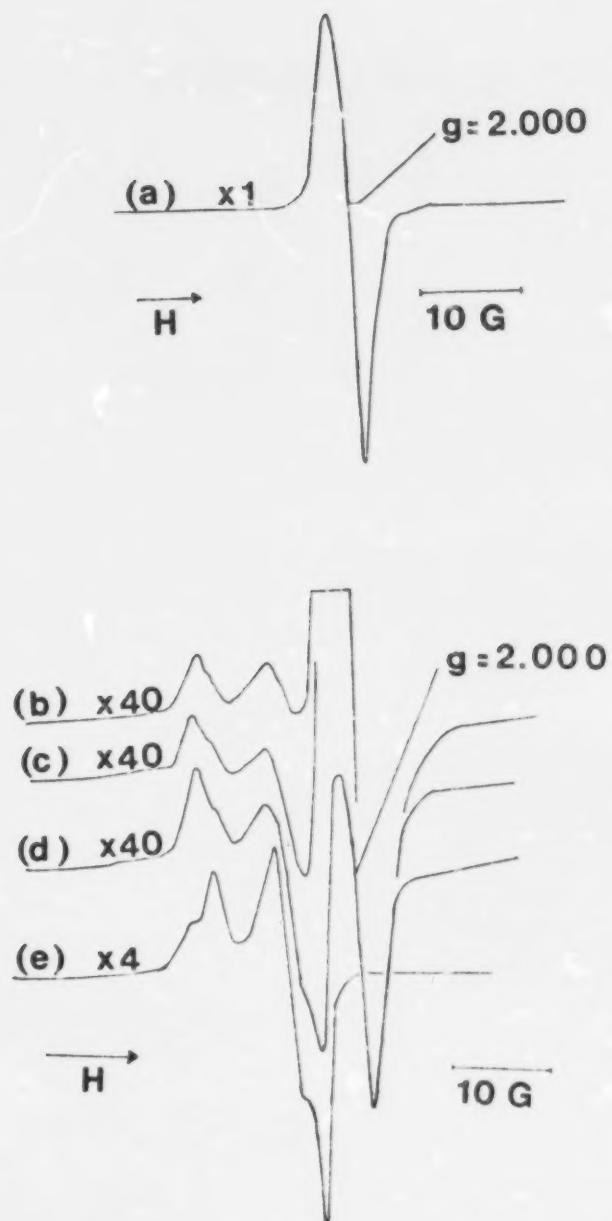


Figure 2. The development of the SO_2^- spectrum from the S-center on MgO pretreated at 500° . (a) Original S-center; (b), (c), (d), increase in intensity of SO_2^- signal with concomitant decrease in intensity of S-center signal; (e) final SO_2^- spectrum.

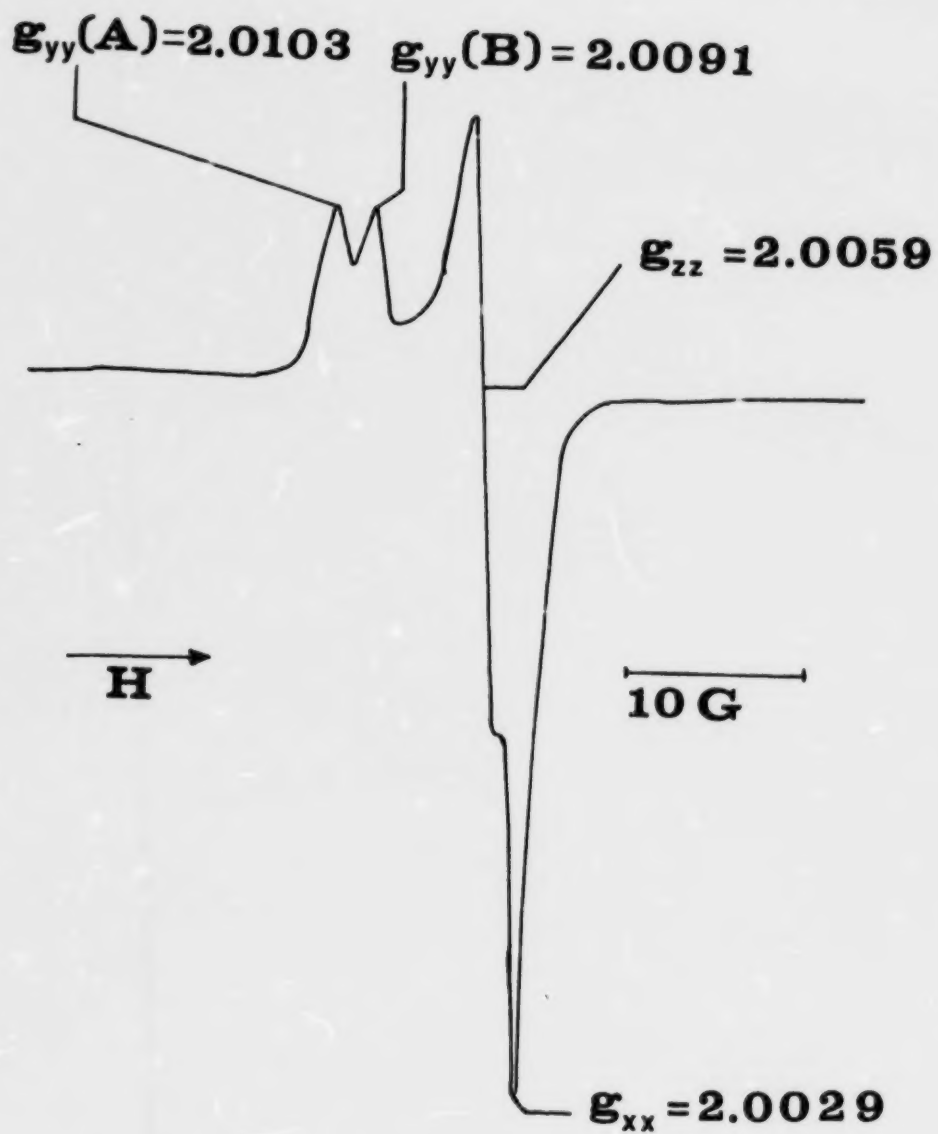


Figure 3. SO_2 on MgO pretreated at 800° .

200° for 2 hr under 1×10^{-5} Torr. A temperature of 400° was necessary to remove SO_2^- (A).

Not all of the adsorbed SO_2 is converted into SO_2^- . Analogous to the results on TiO_2 ¹ the majority of the SO_2 molecules adsorb in a nonparamagnetic form. Indeed, after the MgO was degassed for several hours at 500° under vacuum in order to remove completely the SO_2^- species, and subsequently submitted to uv irradiation, also under vacuum, the SO_2^- spectra reappeared. When the irradiation was performed under a H_2 atmosphere, only the SO_2^- (A) species appeared. The existence of nonparamagnetic SO_2 was further shown by infrared spectroscopy.

The ratio SO_2^- (A) is also influenced by whether the uv irradiation is applied before or after the SO_2 adsorption. If no S-centers were produced prior to the SO_2 adsorption, but uv irradiation was applied after the SO_2 was adsorbed on MgO, the formation of SO_2^- (B) was strongly favored, even when MgO was previously pretreated at 800°. SO_2^- (A) can only be seen as a shoulder on the low-field side of SO_2^- (B). Moreover, SO_2 adsorbed on MgO without uv irradiation, either before or after the adsorption, gave rise to small amounts of SO_2^- . The amounts increase with increasing pretreatment temperature with both SO_2^- species being present. It was thought that this electron transfer from the solid to the SO_2 may create V-type centers; however, attempts to detect them failed.

SO_2 can also be adsorbed on low-surface area MgO after uv irradiation. Both SO_2^- species are present with a SO_2^- (B) : SO_2^- (A) ratio equal to one-half.

Table 1 summarizes the g values for SO_2^- adsorbed on MgO.

Table 1: PRINCIPAL g VALUES FOR SO_2^- ADSORBED

ON MgO AND IN OTHER MATRICES

	g_{yy}	g_{zz}	g_{xx}
SO_2^- (A) ^a	2.0097	2.0052	2.0028
SO_2^- (B) ^a	2.0078	2.0053	2.0014
SO_2^- on TiO_2 ¹	2.005	2.001	2.001
$\text{K}_2\text{S}_2\text{O}_5$ ¹²	2.012	2.0057	2.0019
Na_2SO_4 ¹³	2.0218	2.0076	2.0069
$\text{Na}_2\text{S}_2\text{O}_5$ ¹⁴	2.0102	2.0057	2.0024
KCl ¹⁵	2.0100	2.0071	2.0025
KBr ¹⁵	2.0100	2.0075	2.0050

^a Every g value is an average of seven independent measurements.

They are compared with the values obtained for SO_2^- in other environments.

Sulfur-33 and Oxygen-17 Hyperfine Splittings

The ^{33}S (nuclear spin 3/2) hyperfine lines for either of the two SO_2^- species could be determined by a suitable choice

of the experimental conditions according to the results reported above. By pretreatment of MgO at 500° spectra were obtained with SO_2^- (B) predominantly present. Heating MgO at 800° gave SO_2^- (B) and SO_2^- (A) in approximately equal amounts. Upon subsequent degassing at 200° only SO_2^- (A) remained.

Table 2: PRINCIPAL VALUES OF THE ^{33}S AND ^{17}O
HYPERFINE TENSORS (GAUSS) OF SO_2^- ADSORBED ON
MGO AND IN OTHER MATRICES

	^{33}S		
	g_{xx}	g_{yy}	g_{zz}
SO_2^- (A)	59 ± 1	$(6.6 \pm 2)^a$	9.4 ± 1
SO_2^- (B)	55 ± 1	$(6.6 \pm 2)^a$	9.4 ± 1
$\text{K}_2\text{S}_2\text{O}_5^{12}$	58 ± 0.5	4 ± 4	4 ± 4
KCl^{15}	52.5 ± 1	8.6 ± 1	7.1 ± 1
KBr^{15}	54.3 ± 1	7.1 ± 1	7.1 ± 1

	^{17}O		
	g_{xx}	g_{yy}	g_{zz}
SO_2^- (A)	36 ± 1	$(3 \pm 3)^a$	$(3 \pm 3)^a$
SO_2^- (B)	29 ± 1	$(3 \pm 3)^a$	$(3 \pm 3)^a$
$\text{K}_2\text{S}_2\text{O}_5^{12}$	30 ± 0.5	3 ± 3	3 ± 3
KCl^{15}	...	...	...
KBr^{15}	...	...	...

^a Estimated from other work. ^{12,15}

Comparison of the different spectra obtained in this way enabled us to distinguish between the ^{33}S hyperfine splitting constants of SO_2^- (B) and SO_2^- (A) as indicated in Figure 4 and summarized in Table 2.

The lines corresponding to the x direction are clearly resolved for $^{33}\text{SO}_2^-$ (A) and $^{33}\text{SO}_2^-$ (B); however, the hyperfine lines corresponding to the y and z directions overlap with the $^{33}\text{SO}_2^-$ spectrum. Of the four lines separated by a_{zz} and centered around g_{zz} only the two extreme lines may be observed as small peaks on the tails of the $^{32}\text{SO}_2^-$ spectrum. From the separation between these two lines we calculated $a_{zz} = 9.4 \pm 1$ G. This value should be regarded as a maximum limit to a_{zz} . The four lines centered around a_{yy} could not be resolved from the SO_2^- spectrum. We adopted, therefore, the arithmetic mean of the values of a_{yy} reported by other authors:^{6,7} $a_{yy} = 6.6 \pm 2$ G. A nearly axially symmetric ^{33}S hyperfine tensor is obtained in agreement with previous work.^{12, 15}

The experimental procedure used to obtain the ^{17}O (nuclear spin 5/2) hyperfine tensor is the same as for $^{33}\text{SO}_2^-$. Due to the larger number of lines and the overlap with the $\text{S}^{16}\text{O}_2^-$ spectrum, a_{yy} and a_{zz} could not be calculated from the experimental spectra. Therefore we adopted Reuveni's value¹² of 3 ± 3 G. The spectra are given in Figure 5 and the ^{17}O hyperfine-splitting constants in Table 2.

SO_3^- ON MAGNESIUM OXIDE

Upon addition of excess molecular oxygen to adsorbed SO_2^- it was observed that the spectrum of SO_2^- decreased and a nearly isotropic line with $g = 2.0034 \pm 0.0003$ was formed. Evidence will subsequently be given for the assignment of the

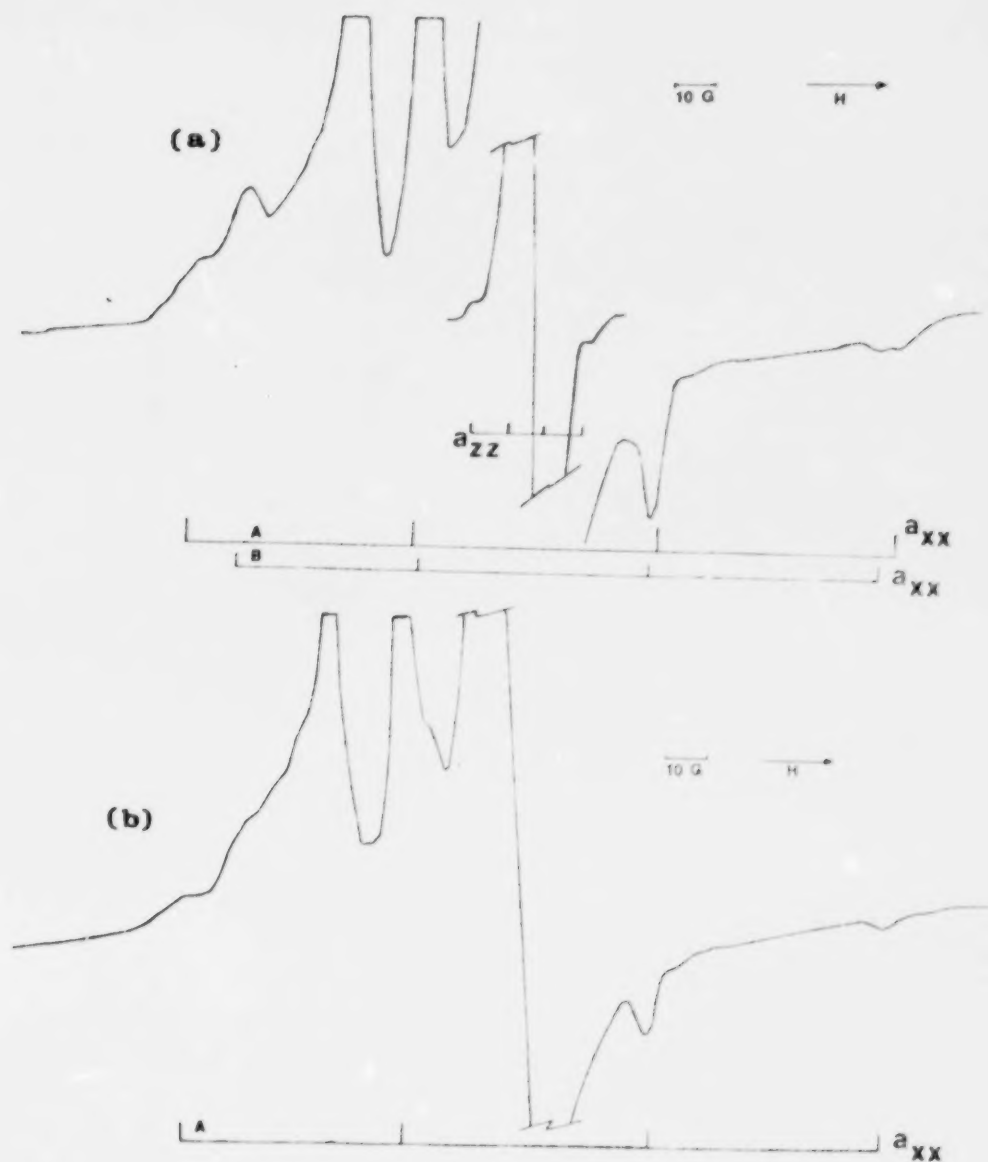


Figure 4. (a) $^{33}\text{SO}_2$ on MgO pretreated at 800° . Both $^{33}\text{SO}_2$ (A) and $^{33}\text{SO}_2$ (B) are present. (b) $^{33}\text{SO}_2$ on MgO pretreated at 800° , followed by subsequent degassing at 200° , only $^{33}\text{SO}_2$ (A) is clearly present.

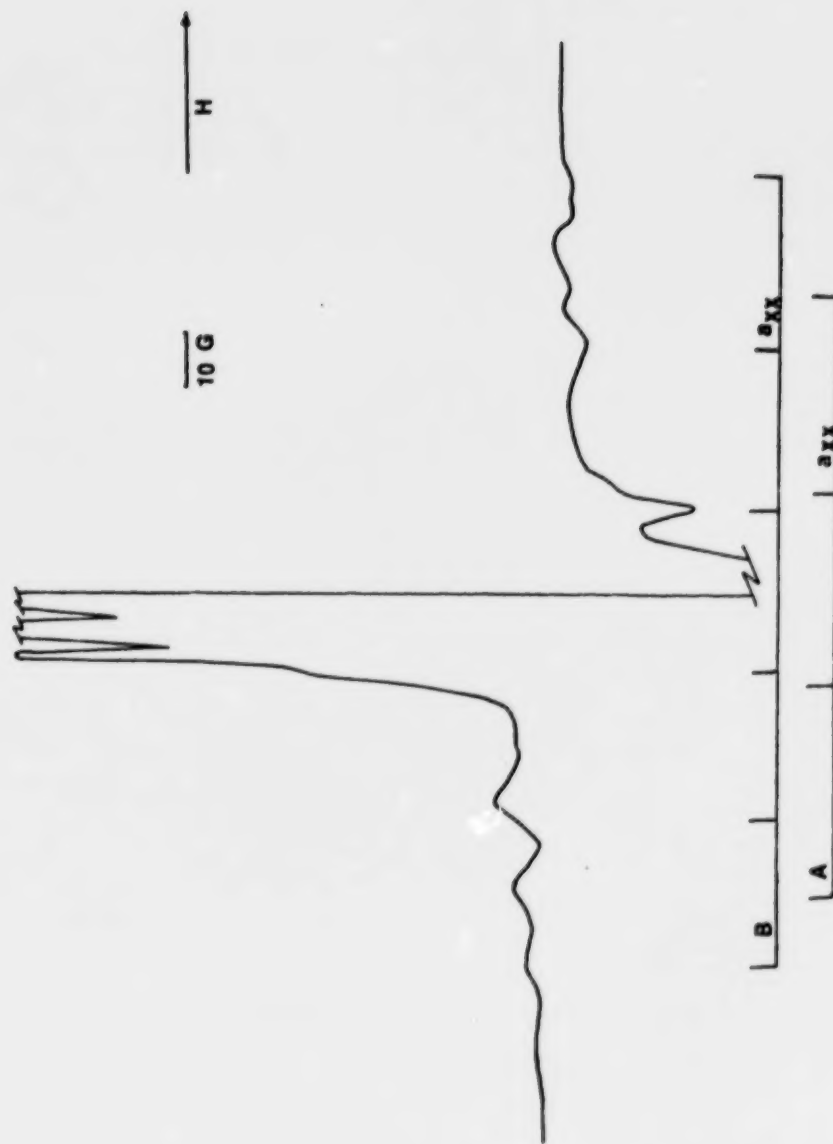


Figure 5. $S^{16}O^{17}O^-$ on MgO pretreated at 800°.

new spectrum to the SO_3^- ion. The formation of SO_3^- was not reversible, i.e., the original SO_2^- signal could not be restored by evacuating the sample at room temperature for over 4 hr. It should be noted, however, that some SO_2^- remained unreacted as indicated by the g_{yy} component which could still be detected, though it was greatly reduced in amplitude.

The rate and extent of the reaction increased with an increased concentration of the initial SO_2^- ion. The SO_3^- ion could be generated from SO_2^- produced from S centers; however, the reaction was more extensive if SO_2 was first allowed to react with the ozonide ion to form a much higher SO_2^- concentration. Upon addition of SO_2 , the symmetric line at $g = 2.0034$ appeared directly. In the latter case no additional O_2 was needed since it is photochemically produced from N_2O . When excess oxygen formed during the uv irradiation of N_2O was removed prior to absorption of SO_2 , only SO_2^- was observed and no oxidation occurred unless O_2 was added back to the system.

The oxidation of SO_2^- to SO_3^- was difficult on samples degassed at 850° . This may be related to a decrease in the concentration of one type of SO_2^- ion, or to a decrease in the concentration of certain diamagnetic ions as will be discussed in a subsequent section.

By using SO_2 enriched to 25% in ^{33}S ($I = 3/2$) four distinct hyperfine lines were observed. These lines in addition to the ^{32}S spectrum are depicted in Figures 6a and 6b. As noted by other investigators^{3,4} the outer lines are shifted about 3 G downfield and the inner lines

about 8 G downfield with respect to the $^{32}\text{SO}_3^-$ line. This shift in the hyperfine components is predicted by second-order terms in the spin Hamiltonian. The shape of the hyperfine spectra varied significantly with changes in the sample temperature. The spectrum of Figure 6a was recorded with the sample at 77°K, whereas the spectrum of Figure 6b was recorded with the sample at room temperature. In both cases it was relatively easy to saturate the spin system with microwave power. From the shape of the hyperfine lines of Figure 6 the values of $a_{||}$ and $a_{\perp}$ were determined. The principal values of the hyperfine tensors are given in Table 3.

Table 3: EPR PARAMETERS FOR SO_3^-

	g	$a_{ }, \text{G}$	$a_{\perp}, \text{G}$
SO_3^- on MgO (77°K)	2.0034 ± 0.0003	147 ± 2	102 ± 2
SO_3^- on MgO (25°)	2.0034 ± 0.0003	102 ± 2	121 ± 2
SO_3^- in $\text{K}_2\text{CH}_2(\text{SO}_3)_2^3$	2.0036 ± 0.0007	153 ± 1	112 ± 1
SO_3^- in taurine ⁴	2.0035 ± 0.0004	135 ± 4	99 ± 4

Under conditions of high modulation amplitude and gain it was even possible to detect the hyperfine structure from SO_3^- containing natural sulfur, which has only 0.74% sulfur-33. This means that the presence of this ion may be confirmed without resorting to the use of enriched SO_2 .

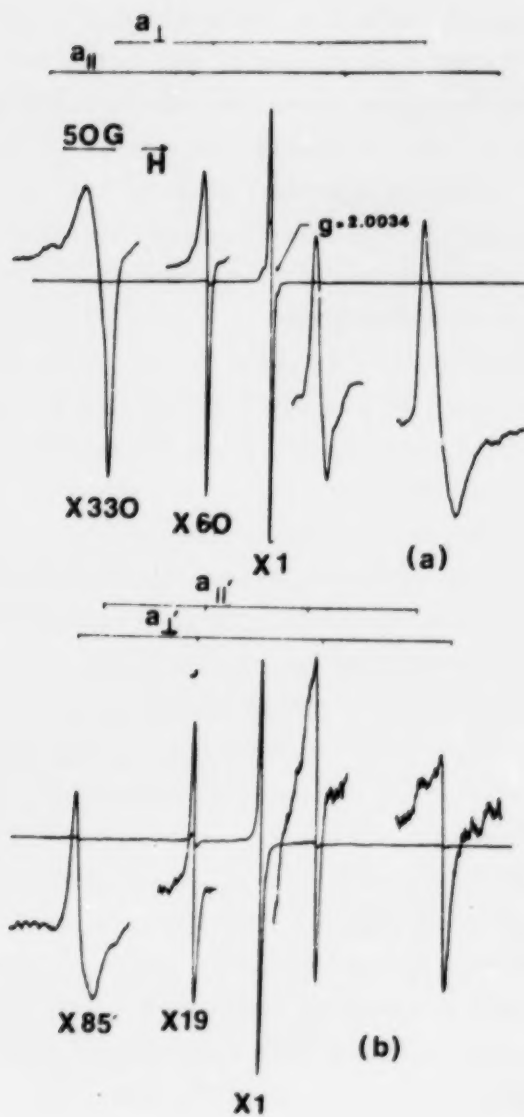


Figure 6. EPR spectrum of SO_3 on MgO : (a) recorded at 77°K , (b) recorded at 25° .

It is perhaps worthwhile to mention that O^- did not react with SO_2 to form SO_3^- . This result was rather surprising in view of the observations that O^- reacts with O_2 forming O_3^- , with CO forming CO_2^- , with C_2H_4 forming $C_2H_4O^-$, and with CO_2 forming CO_3^- . In this experiment O^- was first produced from N_2O and SO_2 was condensed above the sample which was at 77°K. The sample was allowed to warm progressively to higher temperatures and the resulting spectra indicated that O^- reacted with SO_2 forming SO_2^- . The same electron transfer step was detected upon treating SO_2 with adsorbed O_2^- .

COS^- AND CS_2^- ON MAGNESIUM OXIDE

The spectrum of COS^- is shown in Figure 7a along with the principal g-values. By analogy with the CO_2^- molecule ion, the z direction is taken as the symmetry axis and the x direction is taken perpendicular to the plane of the molecule. The low-field spectrum was formed independently from the COS^- spectrum and it had different saturation characteristics. This spectrum is attributed to a sulphur radical produced by the dissociation of COS^- at certain sites. The COS^- species was unstable above -135°C, and at room temperature the characteristic spectrum of a CO complex on MgO was observed¹⁶.

The spectrum of CS_2^- is shown in Figure 7b. The g-values are nearly identical to those reported for CS_2^- formed by reacting CS_2 with alkali metals¹⁷. Again, another spectrum was observed at lower fields. The spectrum of CS_2^- grew slowly at 77°K even though the color change of the MgO indicated a rapid transfer of the electrons at -78°C. A similar phenomenon was also observed for COS^- , but not for CO_2^- at room temperature. It is conceivable that dianions are

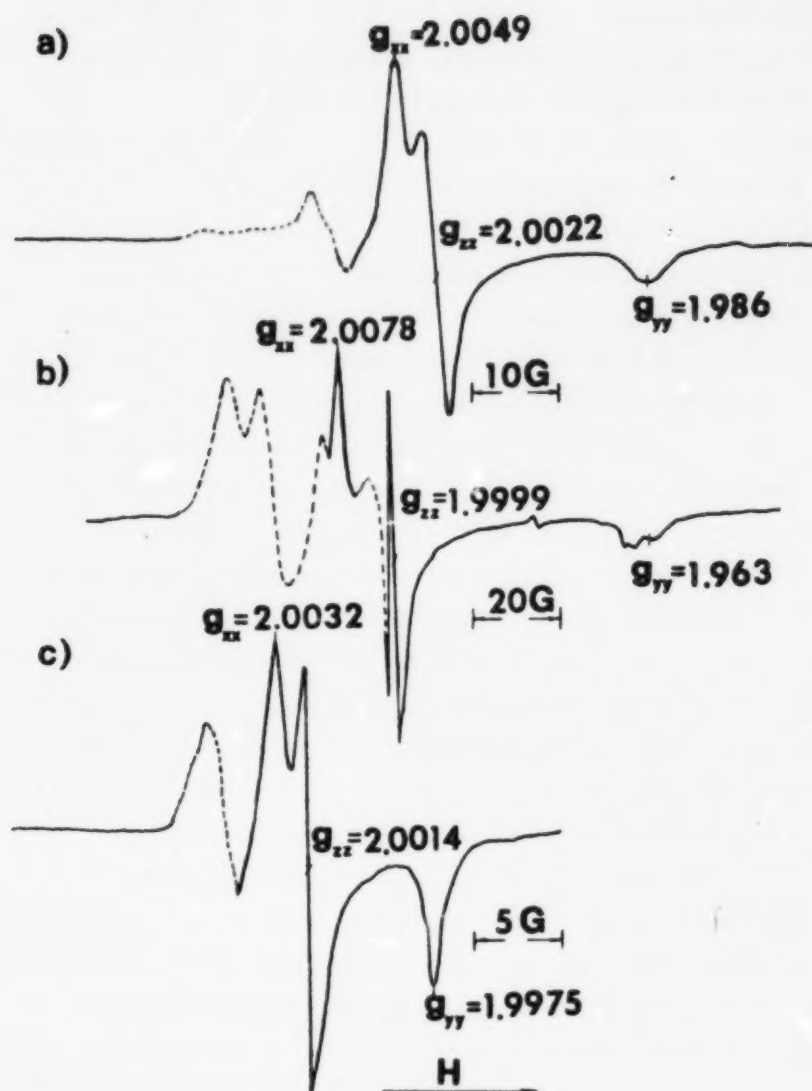


Figure 7. EPR spectra of (a) COS^- on MgO ; (b) CS_2 on MgO and (c) CO_2 on MgO . The spectra of other species are represented by dashed lines.

first formed and that these slowly dissociate to form the singly charged ion.

For comparison purposes the spectrum of CO_2^- on MgO is shown in Figure 7c.

S_3^- ON MAGNESIUM OXIDE

Exposing the magnesium oxide to sulfur vapor at temperatures from 25 to 375°C resulted in a series of complex spectra, which are apparently due to polymeric sulfur radicals. As an example, the spectrum following reaction at 375°C is shown in Figure 8. Even for sulfur enriched to 25.5% with ^{33}S no hyperfine structure was observed, apart from that assigned to S_3^- . The absence of hyperfine structure appears to be a typical of such sulfur radicals formed on high surface area solids.¹⁸

Following reaction at temperatures near 400°C a new species strongly dominated the spectrum. The transformation at this temperature was accompanied by the evolution of H_2S from the surface, or D_2S if $\text{Mg}(\text{OD})_2$ was used to prepare the sample. Magnesium oxide did not react with pure H_2S to form the paramagnetic species. The resulting spectrum from non-labeled sulfur is shown in Figure 9a. It may be described in terms of an apparent axial symmetry with $g_{\perp} = 2.043$ and $g_{\parallel} = 2.004$. A small residual peak from the previous spectrum may be observed at $g = 2.052$. There is also evidence from the Q-band spectra that a weak parallel component may be present at $g_{\parallel} = 2.003$. The spectrum recorded at room temperature was a broad symmetric signal with $g = 2.032$. It should be noted that this is essentially equal to $\frac{1}{3}[2(2.043) + 2.004]$, which is the g value expected for complete motional averaging. A weak maximum at $g = 2.048$ and a minimum at $g = 2.003$ were also observed.

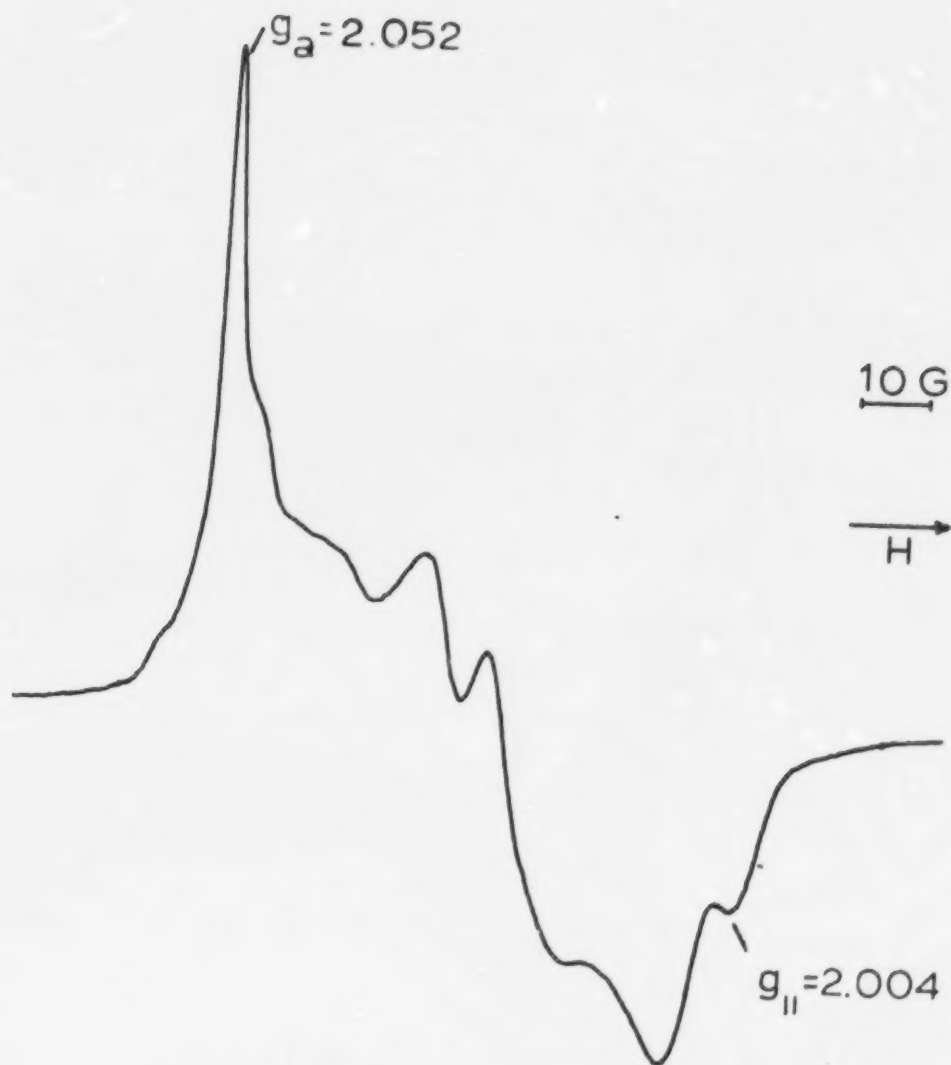


Figure 8. EPR spectrum of sulfur radicals following the reaction of sulfur with partially hydroxylated magnesium oxide at 375°C.

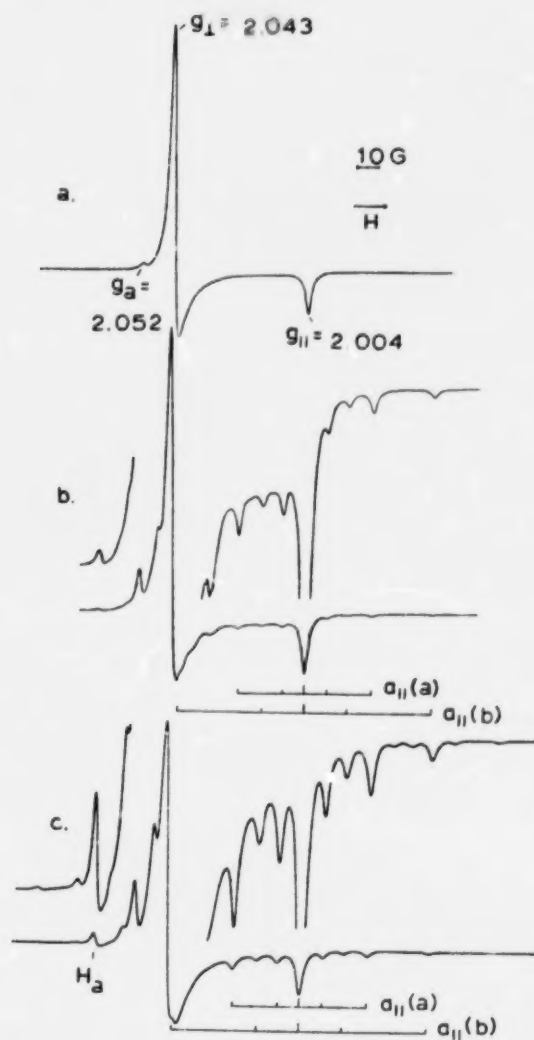


Figure 9. X-band EPR spectrum of S_3^- on MgO : (a) ^{32}S ; (b) sulfur enriched with 9.8% ^{33}S ; (c) sulfur enriched with 25.5% ^{33}S .

Line broadening with molecular oxygen was used to determine whether the radicals were indeed on the surface. Upon exposure of the sample to oxygen at room temperature and then evacuation, the primary spectrum disappeared irreversibly and a weak spectrum similar to that of Figure 8 was observed. When the oxygen was admitted to the original sample at 77°K the spectrum again disappeared, but it reappeared following evacuation of the sample as it was warmed to room temperature. The spectra detected with the sample in the presence of oxygen establish that the weak signal at $g = 2.052$ and the related minimum at $g = 2.003$ are due to a sulfur radical that is not on the surface; whereas, the primary paramagnetic species is on the surface.

The reaction of sulfur enriched to 9.8% in ^{33}S (natural abundance is 0.74%) yielded the spectrum shown in Figure 9b. Two hyperfine quartets with an intensity ratio of about 2:1 are centered on the field corresponding to $g_{||}$. Several components of these quartets could also be detected in the spectrum of nonlabeled sulfur at high gain. Hyperfine lines

Table 4: PRINCIPAL VALUE OF THE g AND HYPERFINE

TENSORS (G) FOR $^{33}\text{S}^-$.

	$g_{ }$ ± 0.001	$g_{\perp}$ ± 0.001	$a_{ }(a)$ $\pm 1 \text{ G}$	$a_{ }(b)$ $\pm 1 \text{ G}$	$a_{\perp}(a)$ $\pm 1 \text{ G}$	$a_{\perp}(b)$ $\pm 1 \text{ G}$
S_3^-/MgO	2.004	2.043	20.7	39.6	3.7	7.5
$\text{S}_3^-/\text{KCl}^{15}$	2.0026	2.0319 ^a	19.3 ^b	51.7	1.4 ^a	10.1 ^a
$\text{S}_3^-/\text{KCl}^{19}$	...	...	19	53	<10	<10

^axx and yy components.

^bThe hyperfine tensor and the g tensor are not diagonalized along the same coordinates.

in the perpendicular region of the spectrum are likewise apparent. The hyperfine lines are even more pronounced following the reaction with sulfur enriched to 25.5% ^{33}S [Figure 9c]. At high gain secondary and tertiary splittings may be observed (Figure 10) in addition to two quartets. The Q-band spectrum of Figure 11 is consistent with the X-band spectrum of Figure 9c.

The experimental hyperfine constants are listed in Table 4. The parallel hyperfine splitting is obvious from the spectra; however, the smaller splitting in the perpendicular region is less well resolved. Computer-simulated spectra were used to establish the optimum set of values and the best spectrum is depicted in Figure 12. The low-field component at H_a is too weak to be a primary hyperfine line. Furthermore, it increased more than the parallel components when the ^{33}S content was changed from 9.8 to 25.5%. This line and the other low-field structure must be associated with still another paramagnetic sulfur species.

INFRARED RESULTS FOR SO_2 ON MAGNESIUM OXIDE

The ir Spectrum of MgO Following Pretreatment at 250-800°

Spectra of MgO at several stages of dehydration were recorded in the regions 1100-1700 cm^{-1} and 3000-3800 cm^{-1} . They are displayed in Figure 13. Heating the sample for 2 hr at 250° resulted in a huge band in the region 3600-3670 cm^{-1} with a shoulder at 3390 cm^{-1} (Figure 13a). In the 1100-1700 cm^{-1} region bands were observed at 1265, 1350, 1410, 1435, 1490 and 1535 cm^{-1} . Following dehydration at 300° the 1535 and 1435 cm^{-1} bands disappeared (Figure 13b). In the OH stretching region the most intense band appeared

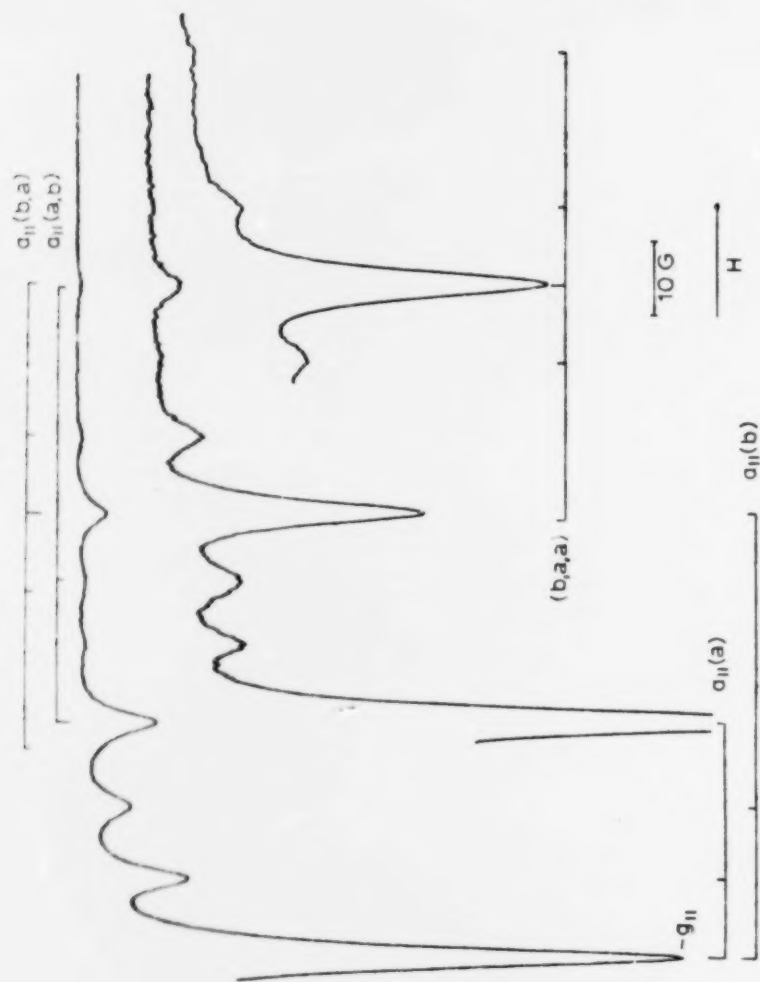


Figure 10. Amplification of hyperfine lines from 25.5% ^{33}S , showing secondary and tertiary splittings.

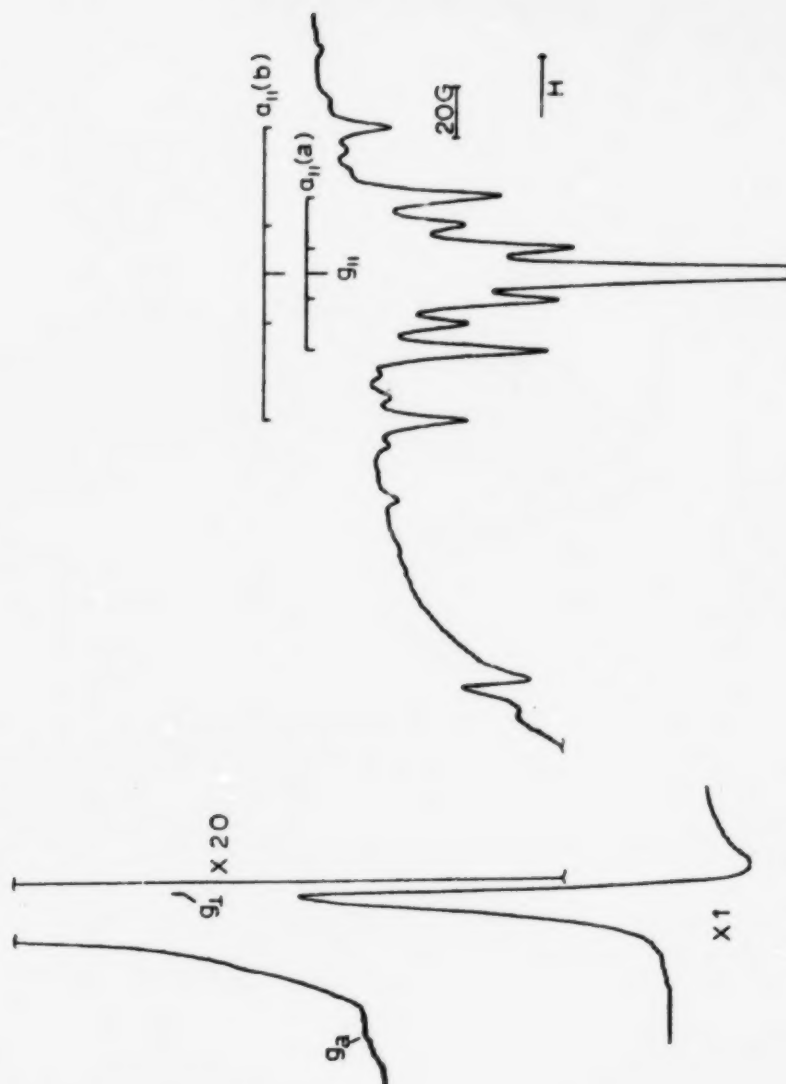


Figure 11. Q-band EPR spectrum of S_3 on MgO . The sulfur was enriched with 25.5% ^{33}S .

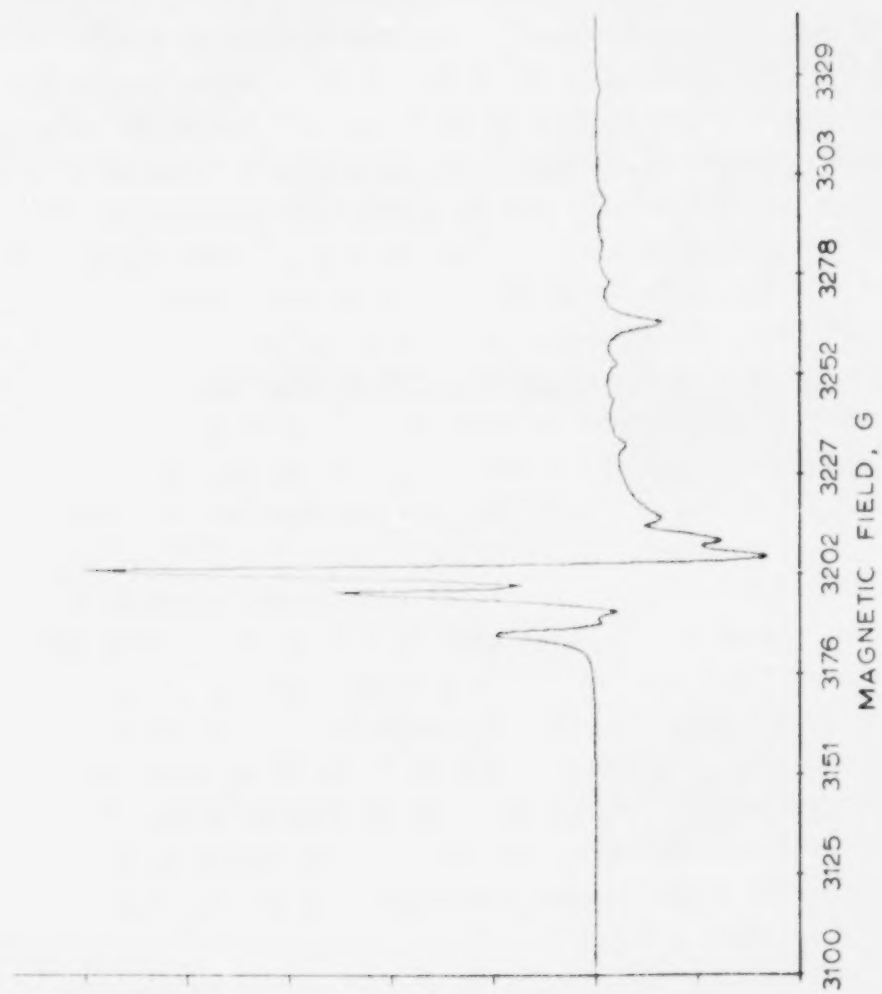


Figure 12. Simulated X-band spectrum for 25.5% ^{33}S enrichment.

at 3750 cm^{-1} with a shoulder at 3725 cm^{-1} . The band in the $3600\text{--}3670\text{ cm}^{-1}$ region was strongly reduced in intensity and three components at 3660 , 3615 and 3530 cm^{-1} may be resolved. The 3390 cm^{-1} band remained unchanged.

At dehydration temperatures above 300° all these bands decreased rapidly in intensity. At 400° only bands at 1265 and 1500 cm^{-1} remained in the $1100\text{--}1700\text{ cm}^{-1}$ region (Figure 13c). Bands occurred also at 3750 cm^{-1} and 3615 cm^{-1} , although strongly reduced in intensity. At 500° , only the 3750 cm^{-1} band was visible in the spectrum (Figure 13d), and at 800° no infrared bands were observed in the regions investigated (Figure 13e). Table 5a summarizes the OH bands observed in the $3000\text{--}3800\text{ cm}^{-1}$ region.

The ir Spectrum of SO_2 Adsorbed on MgO at Room Temperature

Beside the bands due to gaseous SO_2 at 1340 and 1150 cm^{-1} , a broad band was observed between 800 and 1100 cm^{-1} after adsorption of SO_2 . The 3750 cm^{-1} band disappeared but a new broad band developed around 3655 cm^{-1} . The $3725\text{--}3730\text{ cm}^{-1}$ shoulder remained unaltered. Bands were always present at 3575 and around 3450 cm^{-1} but were not always clearly resolved because of their broadness. These features were independent of the pretreatment temperature, except for the 800° pretreatment where no detectable amounts of OH groups were left on the MgO surface. Figure 14a gives an example of the spectra obtained following removal of SO_2 by evacuating at room temperature for 20 min. The MgO sample had been pretreated at 500° .

The Desorption and Reaction of SO_2 at Elevated Temperatures

Figures 14b-e give typical spectra from the desorption and reaction of SO_2 with the surface upon heating the sample

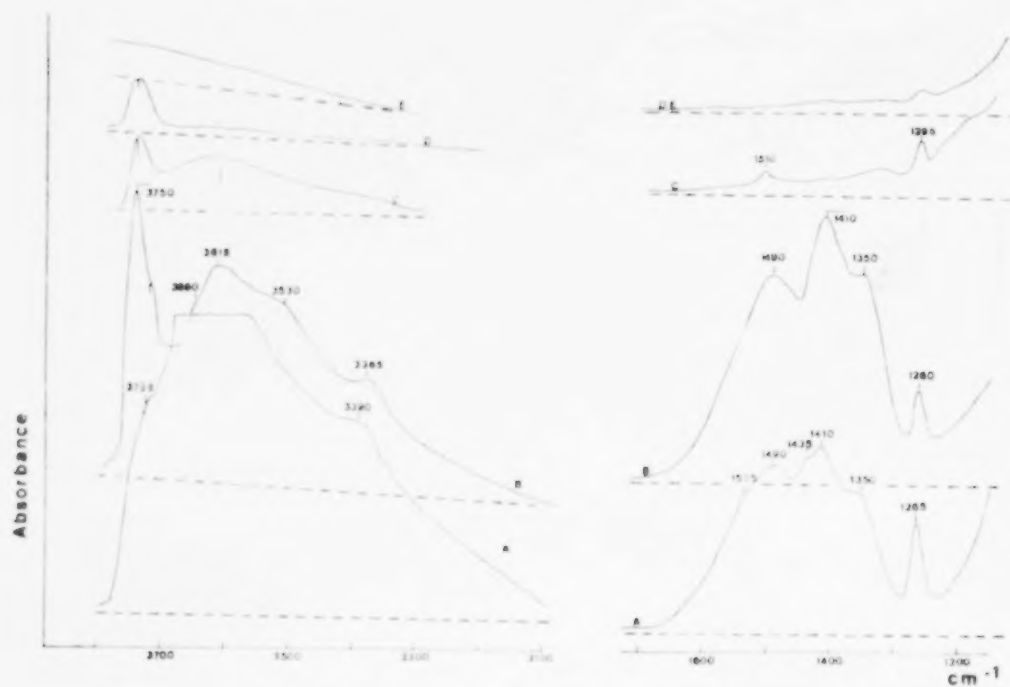


Figure 13. The infrared spectra of MgO at several dehydration temperatures: A. after 2 hr heating at 250°; B. after 2 hr heating at 300°; C. after 2 hr heating at 400°; D. after 2 hr heating at 500°; E. after 2 hr heating at 800°.

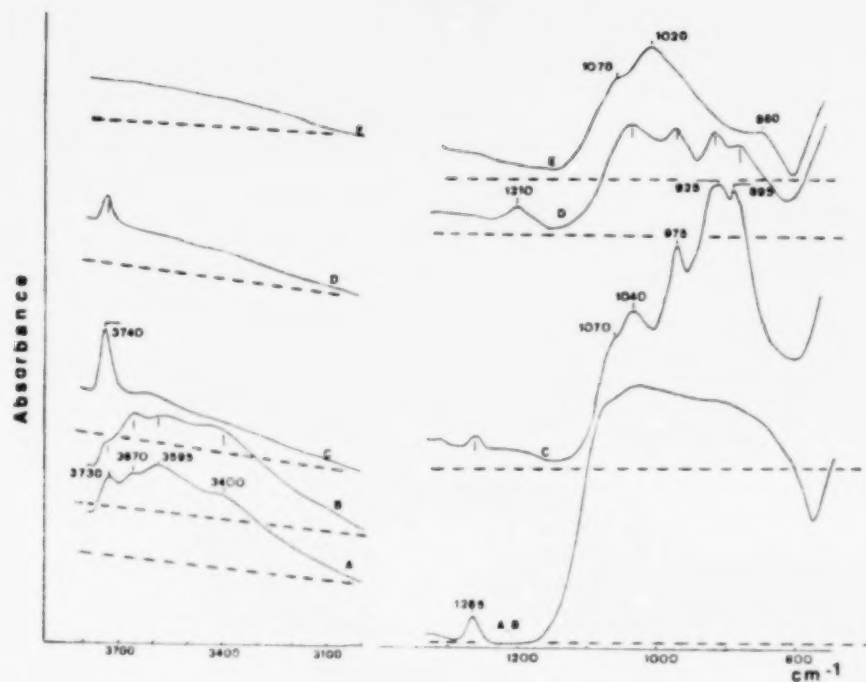


Figure 14. The infrared spectra of SO_2 and its reaction products adsorbed on MgO after degassing in vacuo (MgO pre-treated at 500°): A. at room temperature for 20 min; B. at 220° for 1.5 hr; C. at 420° for 2 hr; D. at 600° for 2 hr; E. at 800° for 2 hr.

Table 5: FREQUENCIES OF THE OBSERVED IR BANDS AND
THEIR ASSIGNMENT

A. OH band spectrum of MgO

Pretreat- ment tem- perature °C	Frequency (cm ⁻¹)	Assignment
300	3750	Free, accessible OH
	3725	Partially inaccessible OH
	3615	Hydrogen bonded OH
	3660	OH group in Mg(OH) ₂
	3530	OH group in Mg(OH) ₂
	3390	OH group in Mg(OH) ₂

B. Bands formed during desorption of SO₂ under vacuum

Degassing temper- ature °C	Frequency (cm ⁻¹)	Assignment
300-500	895	SO ₃ ²⁻ (A)
	925	SO ₃ ²⁻ (A)
	975	SO ₃ ²⁻ (A), SO ₃ ²⁻ (B)
	1040	SO ₃ ²⁻ (B)
	1070	SO ₃ ²⁻ (B)

Table 5 (Continued)

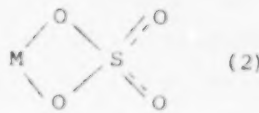
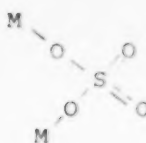
Degassing temper- ature °C	Frequency (cm ⁻¹)	Assignment
800	860	SO ₄ ²⁻
	1020	SO ₄ ²⁻
	1070	SO ₄ ²⁻

C. Bands formed during reaction of adsorbed SO₂ with O₂

Reaction tempera- ture °C	Frequency (cm ⁻¹)	Assignment
400	3740-3750	Free OH
	3640	Mg-OH
		SO ₃
	3430	Mg-OH
		SO ₃
	1345	SO ₃
	1060	
	1240	
	1120	
	1060	
	980	

(1)

Table 5 (Continued)

	1290	
	1175	
	1015	
	910	
	1195	
	1120	
	1045	
	980	
800	1390	
	1360	
	1050	
	1220	
	1170	
	1050	
	950	

to increasingly higher temperatures under dynamic vacuum. After heating 1.5 hr at 220° under vacuum no changes occurred in the 800-1100 cm^{-1} region. The bands in the OH stretching region were better resolved and occurred at 3400, 3600, 3670 and 3730 cm^{-1} (Figure 14b). The latter was increased somewhat in intensity. Further heating for 2 hr at 420° restored the 3740-3750 cm^{-1} band, while the other bands in the OH region disappeared (Figure 14c). The 800-1100 cm^{-1} region was completely altered. Five intense bands were resolved: two partially overlapping bands at 895 and 925 cm^{-1} , a band at 975 cm^{-1} and a band at 1040 cm^{-1} with a shoulder at 1070 cm^{-1} . Up to 500° this five-band spectrum was unaltered.

Above 500° all the bands decreased strongly in intensity as seen in Figure 14d. At 800° no OH bands were left in the 3300-3800 cm^{-1} region and three broad bands at 860, 1020, and 1070 cm^{-1} remained in the 800-1100 cm^{-1} region, regardless of the pretreatment of the MgO sample. A summary of the bands observed under various conditions and their assignments, as explained in the discussion, are given in Table 5b.

A sample pretreated at 330° behaved essentially in the same manner. Its OH bands at 3750 and 3615 cm^{-1} were shifted to lower frequencies at 3655, 3590 and 3400 cm^{-1} . Desorption of SO_2 at 300° for 2 hr restored the two original OH bands. At the same time the five-band spectrum appeared in the 800-1100 cm^{-1} region with an additional weak band at 955 cm^{-1} . The latter disappeared after degassing at 500°.

For MgO pretreated at 800° the same five-band spectrum occurred in the 800-1100 cm^{-1} region at only 300°, although strongly reduced in intensity with respect to the samples

pretreated at 330 and 500°. This reduction in intensity is probably due to a loss in surface area. Some overlapping occurred with the bands at 1020, 1070 and 860 cm^{-1} . As a consequence, the band at 1040 cm^{-1} was not resolved. The bands at 1070 and 1020 cm^{-1} appeared more intense than the bands at 975, 925 and 895 cm^{-1} . This is the reverse of the behavior observed for the samples pretreated at 330 and 500°. The infrared spectrum of SO_2 adsorbed and reacted even at 300° on MgO pretreated at 800° has the characteristic features of SO_2 reacted at 800° on MgO pretreated at 500°.

The Reactivity of Adsorbed SO_2 with O_2

After desorption of SO_2 under vacuum at 500° the residual adsorbed SO_2 species were allowed to react with O_2 at 200° and at increasingly higher temperatures up to 800°. The equilibration time at each temperature was 2 hr. Figure 15 displays the spectra obtained for MgO pretreated at 500°.

Very little change was observed in the spectra after 2 hr heating at 200°, except for the fact that in the 1100-1400 cm^{-1} region (Figure 15b) bands began to appear at the expense of the bands in the 800-1100 cm^{-1} region. This was clearly evident after the 400° treatment: new bands occurred at 1345, 1290, 1240, 1195, 1175 and 1120 cm^{-1} (Figure 15c). Weak bands appeared at 910 and 980 cm^{-1} while the 1040 cm^{-1} band with its shoulder at 1070 cm^{-1} was replaced by a triplet at 1015, 1045 and 1060 cm^{-1} . Drastic changes occurred also in the OH stretching region where two new bands appeared at 3640 and 3430 cm^{-1} besides the 3750 cm^{-1} band.

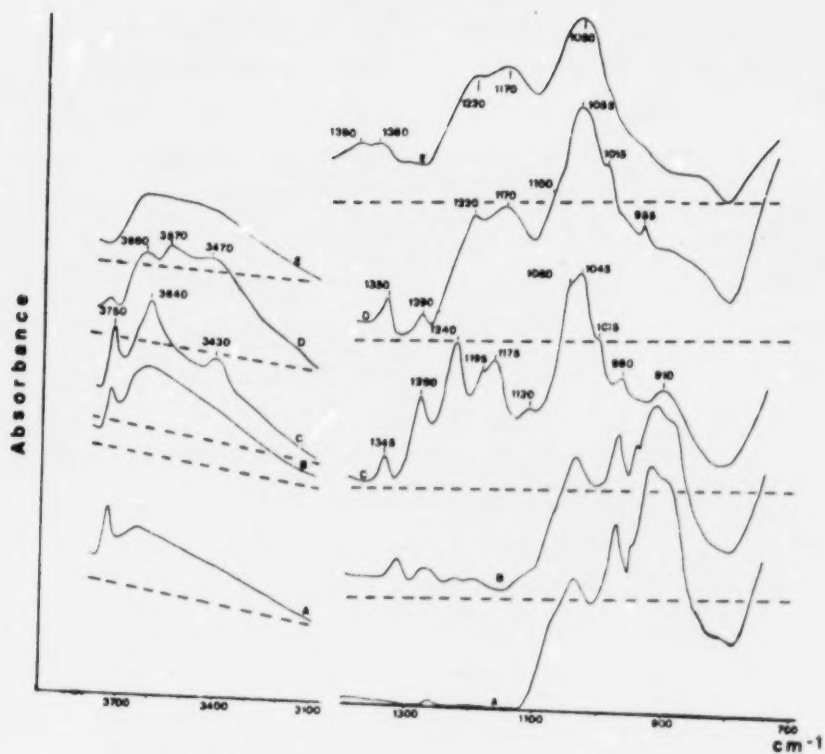


Figure 15. The infrared spectra of sulfite species on MgO before and after reaction with O_2 : A. sulfite on MgO after degassing at 500° in vacuo; B. heating 2 hr in excess O_2 at 200° ; C. after 2 hr in excess O_2 at 400° ; D. after 2 hr in excess O_2 at 600° ; E. after 2 hr in excess O_2 at 800° .

Upon reaction at 600° the bands in the 3100-3800 cm^{-1} region decreased in intensity and became broader (Figure 15d). The 3640 and 3430 cm^{-1} bands were shifted to 3650 and 3470 cm^{-1} , respectively. A new band was evident at 3570 cm^{-1} . The 800-1500 cm^{-1} region was completely changed. The 1290 cm^{-1} band was reduced in intensity, and the four bands in the 1100-1250 cm^{-1} region, originally present after heating at 400°, were replaced by two strong bands at 1220 and 1170 cm^{-1} . The triplet around 1050 cm^{-1} occurred at 1015, 1055, and 1100 cm^{-1} . A weak band at 955 cm^{-1} was the only one remaining at the lower wave numbers.

After 2 hr in oxygen at 800° the OH band spectrum disappeared completely. A broad band was observed around 1050 cm^{-1} (Figure 15e). It is probably composed of three components, equivalent to the triplet described above. Also, the 1220 and 1170 cm^{-1} bands became broader. Two new weak broad bands appeared around 1360 and 1390 cm^{-1} . Table 5c summarizes the observed frequencies and their assignment as explained in the discussion section.

In order to obtain bands with detectable intensity for MgO pretreated at 800°, the SO_2 was not degassed at 500° under dynamic vacuum prior to heating in excess O_2 . No bands were observed in the 3100-3800 cm^{-1} region. After heating 2 hr at 400° in excess O_2 a spectrum was obtained similar to that shown in Figure 15e with the exception of the 1360 and 1390 cm^{-1} bands. Also the band envelopes at 1220 cm^{-1} and 1170 cm^{-1} were more intense than the band envelope at 1050 cm^{-1} . For MgO pretreated at 500° the reverse intensity ratio was observed.

The ir Spectra of MgSO_3 and MgSO_4 on MgO

By way of comparison Figure 16 shows the spectra of MgO doped with solutions of MgSO_3 and MgSO_4 and subsequently degassed at 500° . The MgSO_3 spectrum was not well resolved; however, it resembles qualitatively the spectrum obtained by heating SO_2 on MgO under vacuum at 500° . A broad adsorption occurred in the region $890\text{--}925\text{ cm}^{-1}$ together with bands at 980 cm^{-1} and at 1040 cm^{-1} . The latter had a shoulder at 1080 cm^{-1} . In addition three bands occurred around 1180 , 1220 , and 1265 cm^{-1} .

MgSO_4 gave a better resolved spectrum. A triplet was observed at 1055 , 1040 and 1015 cm^{-1} . Two weak bands were observed at 950 and 980 cm^{-1} . Bands of medium intensity occurred at 1338 , 1260 , 1215 and 1195 cm^{-1} . A shoulder was observed at 1215 cm^{-1} .

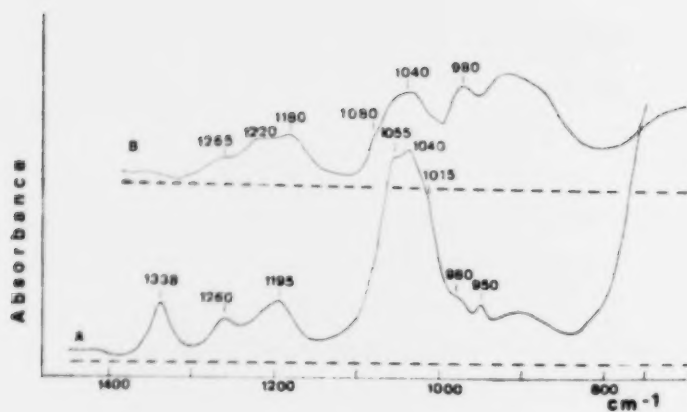


Figure 16. A. Infrared spectrum of MgO doped with Mg SO₄ solution and subsequently degassed at 500° for 2 hr. B. Infrared spectrum of MgO doped with a Mg SO₃ solution and subsequently degassed at 500° for 2 hr.

SECTION VI

DISCUSSION

SO_2^- ON MAGNESIUM OXIDE

The qualitative agreement between the esr spectra obtained with SO_2 adsorbed on MgO before or after uv irradiation of the solid, the similarity of our g values with those of other authors (Table 1), and the hyperfine-splitting data unambiguously reveal that our esr signal is due to SO_2^- . Moreover, the two different signals indicate two slightly different adsorption sites on MgO .

Characterization of the SO_2^- Molecule

SO_2^- has 19 valence electrons. The odd electron occupies a $2b_1$ molecular orbital according to Walsh's diagram.²⁰ Reuveni¹² and Dinse²¹ have given an explicit wave function for this $2b_1$ MO neglecting the sulfur 3d-orbital contribution

$$\psi(2b_1) = c_1 S(3p_x) + \frac{b_1}{\sqrt{2}} O(2p_{x1} + 2p_{x2}) \quad (1)$$

where $1/\sqrt{2}$ is a normalization constant.

The molecular orbital occupied by the odd electron is thus a linear combination of atomic p_x orbitals, perpendicular to the plane of the molecule. According to Reuveni, et al.,¹² one expects the following characteristics for the SO_2^- molecule and its g tensor and hyperfine-splitting tensors: (a) two magnetically equivalent oxygens, (b) axially symmetric ^{17}O and ^{33}S hyperfine tensors with their unique components parallel

to each other and perpendicular to the molecular plane, and (c) along this unique hyperfine direction the g value should be close to the free-electron value. The maximum g value should be along the O-O direction, which is the y direction.

Sulfur and Oxygen Hyperfine Interactions

The ^{33}S and ^{17}O hyperfine tensor may be resolved into an isotropic part (A_{iso}) and a traceless anisotropic part (A) as described in Table 6. The choice of the sign is made so as to be in agreement with A_{iso} for SO_2^- in solution¹² where A_{iso} for $^{17}\text{O} = 8.96 \pm 0.05$ G and A_{iso} for $^{33}\text{S} = 14.67 \pm 0.05$ G.

For the pure 3s orbital of ^{33}S the coupling is 970 G and for the pure 2s orbital of ^{17}O a value of 590 G is reported.^{3,22} Comparing with our values, we conclude that the spin density in the 3s orbital of sulfur and 2s orbital of O is between 1 and 2%. This number is negligibly small and can be accounted for entirely by spin polarization. The wave function adopted in the previous section can therefore be considered as a good representation of the molecular orbital of the odd electron, at least in the LCAO scheme.

Table 6: ISOTROPIC AND ANISOTROPIC PARTS OF THE ^{33}S
AND ^{17}O HYPERFINE TENSORS (GAUSS)

	A_{iso}	A_{xx}	A_{yy}	A_{zz}
$^{33}\text{SO}_2^-$ (A)	14.3 ± 2	44.7 ± 2	-20.9 ± 3	-23.7 ± 2
$^{33}\text{SO}_2^-$ (B)	13 ± 2	42 ± 2	-19.6 ± 3	-22.4 ± 2
$\text{S}^{16}\text{O}^{17}\text{O}^-$ (A)	10 ± 4	26 ± 4	-13 ± 5	-13 ± 5
$\text{S}^{16}\text{O}^{17}\text{O}^-$ (B)	7.7 ± 4	21.3 ± 4	-10.7 ± 5	-10.7 ± 5

The coefficients b_1 and c_1 of the $2b_1$ molecular orbital may then be calculated by comparing the experimental values of A_{xx} with the theoretical values for an odd electron in a p orbital on ^{33}S and ^{17}O , respectively. The theoretical value of A_{xx} for ^{33}S was calculated with the aid of the numerical value, $\langle r^{-3} \rangle_s = 3.41 \times 10^{25} \text{ cm}^{-3}$, reported by Dinse and Möbius.²¹ Using the value of $\langle r^{-3} \rangle_o = 3.36 \times 10^{25} \text{ cm}^{-3}$ ²² the theoretical value of A_{xx} for ^{17}O was also calculated. Table 6 lists the spin densities on $\text{S}(3p_x)$ and $\text{O}(2p_{x1} + 2p_{x2})$ together with the total spin density calculated in this manner. It must be remarked that the spin density on the oxygen reported here is higher than for SO_2^- trapped in a solid matrix, while the values for ^{33}S are nearly the same. This difference, however, may only be due to the approximations made during the calculation.

Table 7: $2b_1$ MO COEFFICIENTS AND SPIN DENSITIES
ON S AND O FOR SO_2^- ON MGO

	SO_2^- (A)	SO_2^- (B)
c_1	0.86	0.84
b_1	0.52	0.48
c_1^2	0.75	0.71
b_1^2	0.27	0.23
$c_1^2 + b_1^2$	1.02	0.94

The g Tensor

The dominant contribution to the g shift comes from mixing the $2b_1''$ orbital with the $3a_1'$ and $2b_2'$ orbitals.^{5,7}

The wave functions of these orbitals are

$$\begin{aligned}\psi(3a_1') = c_2 S(3p_z) + c_4 S(3s) + \frac{b_2}{\sqrt{2}} O(2p_{z1} + 2p_{z2}) + \\ \frac{b_2}{\sqrt{2}} O(2p_{y1} - 2p_{y2})\end{aligned}\quad (2)$$

and

$$\begin{aligned}\psi(2b_2') = c_3 S(3p_y) + \frac{b_4}{\sqrt{2}} O(2p_{z1} - 2p_{z2}) + \\ \frac{b_5}{\sqrt{2}} O(2p_{y1} + 2p_{y2})\end{aligned}\quad (3)$$

Exact values for the different coefficients occurring in these wave functions are not available. We assume, as Reuveni did, $c_3 = b_3 = 0$. The ratio c_2/c_4 can be obtained from the bond angle of SO_2^- with the aid of Coulson's relation between the degree of hybridization and bond angle.²³ The bond angle of SO_2^- is not available. We adopted, therefore, the angle of SO_2 in the $^3B_1$ state as calculated by Brand and coworkers.²⁴ This value is 126.2° and gives $c_2/c_4 = 1.71$.

Assuming with Reuveni that $c_2^2 = 2b_2^2$ and that $b_4 = b_5$, and applying the normalization condition of the wave functions $\psi(3a_1)$ and $\psi(2b_2)$ including overlap, one obtains the following values for the coefficients: $c_4 = 0.36$, $c_2 = 0.63$, $b_2 = 0.40$, and $b_4 = b_5 = 1/\sqrt{2}$. Then the deviations from the free-electron g value are

$$\Delta g_{xx} = 0 \quad (4)$$

$$\Delta g_{yy} = \frac{2(c_1 c_2 \lambda_s + b_1 b_2 \lambda_0)(c_1 c_2 + b_1 b_2)}{E(2b_1'') - E(2b_2')} \quad (5)$$

$$\Delta g_{zz} = \frac{2b_1^2 b_2^2 \lambda_0}{E(2b_1'') - E(2b_2')} \quad (6)$$

where $\lambda_s = 386 \text{ cm}^{-1}$ is the spin-orbit constant for S and $\lambda_0 = 157 \text{ cm}^{-1}$ is the spin-orbit coupling constant for O. The energy differences in the denominators have been estimated by Dinse and Möbius.

$$E(3a_1') - E(2b_1'') = 34,500 \text{ cm}^{-1} \quad (7)$$

$$E(2b_2') - E(2b_1'') = 38,500 \text{ cm}^{-1} \quad (8)$$

We obtain then for SO_2^- (A) $\Delta g_{xx} = 0$, $\Delta g_{zz} = 0.0011$, and $\Delta g_{yy} = 0.0140$; whereas, for SO_2^- (B) $\Delta g_{xx} = 0$, $\Delta g_{zz} = 0.0009$, and $\Delta g_{yy} = 0.0136$.

The agreement with experiment is only qualitative in the sense that we predict the right sequence of Δg shifts. No conclusion about the bond angle of SO_2^- can be obtained. We adopted the 126.2° bond angle because we feel that the SO_2^- bond angle is closer to that of the $^3B_1$ excited state of SO_2 than to that of the ground state of SO_2 . A widening of the bond angle of SO_2^- with respect to SO_2 is not unreasonable when one considers Walsh's diagram. The $2b_1''$ molecular orbital increases only slightly in energy in going from 90° to 180° bond angle. The $4a_1'$ orbital which is the highest filled orbital of SO_2 has a much greater energy increase in going from 90° bond angle to the linear form. A bond angle close to 90° is therefore more likely.

The Nature of the Adsorption Sites

When MgO is degassed and subsequently uv irradiated in a H_2 atmosphere, two different epr signals are developed, corresponding to a pretreatment temperature of 500 and 800°, respectively. The center obtained after the 500° pretreatment has an axially symmetric g tensor and is believed to be an electron trapped at an oxygen ion vacancy. The center after the 800° pretreatment was first ascribed to an electron trapped at an anion-cation vacancy pair by Lunsford and Jayne.² Nelson and coworkers,²⁴ however, showed that this epr signal involves a hydrogen hyperfine splitting and that two centers are present.

The existence of two different paramagnetic centers is clearly confirmed in this work by the presence of two different types of SO_2^- . Moreover, each SO_2^- species retains its same asymmetric g tensor whatever the pretreatment of MgO. This suggests that only the relative number of the two adsorption sites changes with changing pretreatment temperatures.

We think that it is reasonable to ascribe both the electron trapping centers and the SO_2^- adsorption sites to oxygen ion vacancies at the surface. As a working model one may consider that the sites giving rise to SO_2^- (B) are oxygen ion vacancies on the edges of the microcrystals: the centers forming SO_2^- (A) are then oxygen ion vacancies on the flat surface of the microcrystals. The change of their relative number with increasing pretreatment temperature is in agreement with this assignment; that is, one can imagine that the decrease in surface area at 800° is due to a smoothing out of the surfaces of MgO crystallites, thus resulting in a

decrease in the number of edges present on the nonideal crystal surfaces. The number of sites (a maximum of $10^{19}/g$) can easily be accounted for in this manner.

No explicit proof can be offered to show the orientation of SO_2^- with respect to the surface. The odd electron is entirely located on the SO_2^- ion as suggested by our calculations. Since it plays no role in any kind of covalent bond, the bonding forces are purely electrostatic. The oxygen ion vacancies have a positive character and are likely to attract the more electronegative oxygen atoms instead of the sulfur atom. An analogous orientation has been proposed by Bennett and coworkers^{17,25} for CO_2^- and CS_2^- bonded to alkali metals.

SO_3^- ON MAGNESIUM OXIDE

g Tensor

According to a Walsh diagram for AB_3 type molecules, SO_3^- with 25 valence electrons should be pyramidal with C_{3v} symmetry. The filling of the $^2A_1$ ground state should be according to the sequence

$$\dots (1e)^4 (5a_1)^2 (2e)^4 (3e)^4 (1a_2)^2 (6a_1)^1$$

The g tensor should reflect the axial symmetry of the anion. The g shifts for the perpendicular direction would be due to the excitation from the $^2A_1$ ground state to the ^2E state, either as

$$\dots (1e)^4 (5a_1)^2 (2e)^3 (3e)^4 (1a_2)^2 (6a_1)^2$$

$$\text{or as } \dots (1e)^4 (5a_1)^2 (2e)^4 (3e)^3 (1a_2)^2 (6a_1)^2.$$

For the parallel direction g shifts would be due to excitation from the ground state to the $^2A_2$ state

$$\dots (1e)^4 (5a_1)^2 (2e)^4 (3e)^4 (1a_2)^1 (6a_1)^2$$

In terms of energy the $6a_1$ orbital lies well separated from the $2e$, $3e$, and $1a_2$ orbitals; hence, only a small departure of the principal g values from the free electron value is expected. One would predict that $g_{||}$ and $g_{\perp}$ would be slightly greater than 2.0023, which is consistent with the observed value of 2.0034.

Hyperfine Tensor

The hyperfine structure of Figure 6a is in good agreement with that reported for the SO_3^- ion, thus confirming the identification of the ion on magnesium oxide. The tensor has nearly cylindrical symmetry, which is expected for the pyramidal SO_3^- ion. The direction of the unique axis is normal to the plane formed by the three oxygen atoms.

Table 8: COMPARISON OF HYPERFINE COUPLINGS, SPIN DENSITIES, AND
BOND ANGLES FOR SO_3^- IN DIFFERENT ENVIRONMENTS

	SO_3^- on MgO	SO_3^- in $K_2CH_2(SO_3)_2$	SO_3^- in taurine
Isotropic coupling, A_{iso} , G	117	126	111
Anisotropic coupling, $2B$, G	30	27	24
Spin density 3s	0.12	0.13	0.11
3p	0.51	0.46	0.41
OSO angle, degree	112	111	111

The hyperfine tensor may be resolved into its isotropic part, A_{iso} , and anisotropic part, 2β , in the usual manner. Upon assuming that the d orbital contribution to the wave function was negligible, the s and p character of the unpaired electron localized on the sulfur were calculated. Here, values of $A_{iso} = 970$ G for a pure 3s orbital of ^{33}S and $2\beta = 59$ G for a pure 3p orbital were used.³ Results for SO_3^- in different environments are given in Table 8.

The OSO bond angle for this ion was calculated from the equation¹⁵

$$\phi = \cos^{-1} \left[\frac{1.5}{2\lambda^2 + 3} - \frac{1}{2} \right] \quad (9)$$

where λ^2 is the ratio of the p to s character of the unpaired electron on the sulfur. This leads to a calculated bond angle of 112° , which is very similar to that reported by Chantry, et al.¹³ Obviously the crystalline environment does not greatly distort the SO_3^- ion.

The spectrum of SO_3^- in Figure 6b is unique to MgO. It appears to suggest that $a_{\perp} > a_{||}$, which yields a value for the 3p character of only 0.27. This drastic reduction in the 3p character is unlikely in view of the consistent parameters noted in Table 8 for SO_3^- in quite different environments. A more plausible explanation of the spectrum observed at room temperature is evident if one assumes motion in a plane which includes the threefold symmetry axis. A libration such as depicted in Figure 17, would have the effect of averaging $a_{||}$ and one $a_{\perp}$ component giving $a_{\perp}'$. The other $a_{\perp}$ component would become $a_{||}'$. The numerical values of $a_{\perp}'$ and $a_{||}'$ given in Table 8 are in agreement with this model. Such motion could

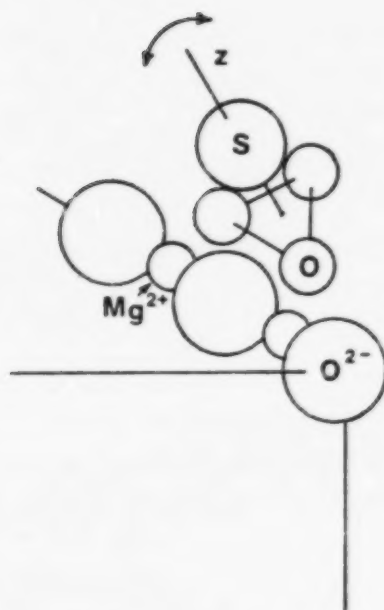


Figure 17. Schematic representation of SO_3 motion on the edge of a MgO crystallite.

easily occur on edges of the MgO crystallites which are approximately $100 \text{ \AA}$ on a side. Similar motion for S_3^- on MgO was detected even at 77°K .

Reaction Mechanism

The epr results reported here clearly establish that SO_2^- may be oxidized to SO_3^- with molecular oxygen. Furthermore, the ease and extent of oxidation depend on the concentration of SO_2^- ions. This concentration effect may be interpreted in terms of a concerted process involving an intermediate such as $\text{SO}_2^- \dots \text{O}-\text{O} \dots \text{SO}_2^-$, although the line width of the epr spectrum indicates that the paramagnetic ions are separated from one another by a distance greater than $5 \text{ \AA}$. It is more reasonable to assume that an intermediate such as $\text{SO}_2^- \dots \text{O}-\text{O} \dots \text{SO}_3^{2-}$ is formed, which then results in SO_3^- and a diamagnetic SO_4^{2-} ion. Experiments currently in progress on other types of surfaces may help to resolve this mechanistic problem.

CO_2^- AND CS_2^- ON MAGNESIUM OXIDE

It is of interest to examine the g-tensor shifts for the series CO_2^- , COS^- and CS_2^- . The largest deviation from the free electron g-value, Δg_{yy} , is associated with a mixing of the $2b_1$ excited state into the $4a_1$ ground state. For CO_2^- the $4a_1$ orbital can be described as

$$\begin{aligned} \psi(4a_1) = & c_1 \psi C(s) + c_2 \psi C(p_z) \\ & + c_3 \psi O(p_z + p_{z'}) + c_4 \psi O(p_y - p_{y'}) + c_5 \psi O(s + s'), \quad (10) \end{aligned}$$

and the $2b_1$ orbital as

$$\psi(2b_1) = d_2 \psi C(p_x) + d_3 \psi O(p_x + p_{x'}). \quad (11)$$

The g shift is given by

$$\Delta g_{yy} = -2(c_2 d_2 \lambda_C + 2c_3 d_3 \lambda_O)(c_2 d_2 + 2c_3 d_3)/\Delta E, \quad (12)$$

where λ_C and λ_O are the one-electron spin-orbit coupling parameters ($\lambda_C = 29 \text{ cm}^{-1}$, $\lambda_O = 151 \text{ cm}^{-1}$, $\lambda_S = 382 \text{ cm}^{-1}$ ²³).

Using the hyperfine data of Ovenall and Whiffen²⁶ for CO_2^- , one may calculate that $c_1 = 0.389$ and $c_2 = -0.586$. The coefficient c_3 can be estimated from the normalization condition

$$c_1^2 + c_2^2 + 2c_3^2 + 2c_4^2 + 2c_5^2 = 1. \quad (13)$$

Since $c_4^2 + c_5^2$ is expected to be nearly zero, a value of $c_3 = 0.5$ results. Using $d_2 = 0.75$ and $d_3 = -0.47$ [7] and $\Delta E = 29,400 \text{ cm}^{-1}$ ²⁷, eq. (3) leads to a value of $\Delta g_{yy} = -0.0052$, in close agreement with $\Delta g_{yy}(\text{obs}) = -0.0049$.

For CS_2^- the hyperfine data of Bennett et al.¹⁷ indicate that $c_1 = 0.280$ and $c_2 = -0.650$. The observation that $c_1^2 + c_2^2$ are of equal magnitude for CO_2^- and CS_2^- is surprising, in view of the difference in electronegativities of O and S. It follows that c_3 is equal to 0.5. Using Bennett's estimation of $\Delta E \approx 10,000 \text{ cm}^{-1}$, and the same d_2 and d_3 as above, one calculates that $\Delta g_{yy} = -0.037$, which compares favorably to $\Delta g_{yy}(\text{obs}) = -0.039$. It is of course necessary to substitute λ_S for λ_O in eq. (1).

Theoretical calculations are more difficult on COS^- because there is no hyperfine data presently available. Since $c_1^2 + c_2^2$ are nearly identical for CO_2^- and CS_2^- , it seems reasonable to take the average of the coefficients for those two ions as an estimate for COS^- . This assumption results in $c_1 = 0.334$, $c_2 = -0.618$, and $c_3 = 0.5$. The second term

in eq. (10) becomes $c_3 d_3 (\lambda_O + \lambda_S)$. Taking $\Delta E = 19,700 \text{ cm}^{-1}$ (averaging ΔE 's from CO_2^- and CS_2^-) and d_2 and d_3 as before, $\Delta g_{yy} = -0.013$, in fair agreement with $\Delta g_{yy} (\text{obs}) = -0.016$. Currently, work is underway to determine hyperfine data for COS^- and CS_2^- on MgO .

S_3^- ON MAGNESIUM OXIDE

The hyperfine structure provides convincing evidence that the principal sulfur species on MgO after the reaction at 400°C is a triatomic sulfur molecule. The 2:1 ratio for the two main quartets indicates that there are twice as many atoms of one type as another type. The presence of tertiary splitting confirms that at least three sulfur atoms are present. Furthermore, assuming the radical is an aba type molecule, the percentages of each labeled atom are in good agreement with the calculated values (Table 9). These percentages were determined from the relative amplitudes of the hyperfine lines.

These observations suggest that the paramagnetic sulfur is either a 19-valence-electron S_3^- ion or a 17-valence-electron S_3^+ ion. The S_3^- ion has been extensively studied in alkali halide single crystals by Schneider et al.¹⁵ and by Suwalski and Seidel.¹⁹ The g and hyperfine tensors for the ion in KCl are reported in Table 4. Here, the z direction is perpendicular to the plane of the molecule and y bisects the $\text{S}_a\text{S}_b\text{S}_a$ angle. If one assumes that the ion on the surface is librating in the xy plane, the g tensor and the hyperfine constants are reasonably close to those reported for S_3^- .

Although there is no reported spectrum for S_3^+ , the 17-electron NO_2 and CO_2^- molecules have been extensively

investigated on MgO and in other media. They are generally characterized by one g value, which is less than g_e . Moreover, the wavefunction of the molecular orbital containing the unpaired electron has considerable s character on the central atom. Both the g and the hyperfine tensors of the sulfur ion are in disagreement with these observations for 17-electron radicals.

Additional support for S_3^- is apparent if one considers the spin density on each sulfur atom. Neglecting any d orbital contribution, the odd electron would occupy the $2b_1$ MO, which has the form

$$|2b_1\rangle = -c_1(2p_z^{Sb}) + c_2(2p_z^{Sa^1} + 2p_z^{Sa^2})\sqrt{2}. \quad (14)$$

The coefficients c_1 and c_2 may be evaluated by resolving the experimental hyperfine tensor into its isotropic and anisotropic components:

$$\begin{bmatrix} -7.5 & & \\ & -7.5 & \\ & & 39.6 \end{bmatrix} = 8.2 + \begin{bmatrix} -15.7 & & \\ & -15.7 & \\ & & 31.4 \end{bmatrix} \quad (15)$$

and

$$\begin{bmatrix} -3.7 & & \\ & -3.7 & \\ & & 20.7 \end{bmatrix} = 4.4 + \begin{bmatrix} -8.1 & & \\ & -8.1 & \\ & & 16.3 \end{bmatrix} \quad (16)$$

Here, the negative signs for the perpendicular components have been chosen in agreement with the results for SO_2^- and

SeO_2^- . For these ions the isotropic term was evaluated directly; hence, the relative signs of the elements in the experimental hyperfine tensor could easily be deduced.¹⁵ Using a theoretical value of 97 G for the isotropic interaction

Table 9: EXPERIMENTAL AND CALCULATED PERCENTAGES

FOR ^{33}S ISOTOPE COMBINATIONS IN $\text{S}_a\text{S}_b\text{S}_a^-$.

	<u>25% ^{33}S</u>		<u>10% ^{33}S</u>	
	Exptl	Calc	Exptl	Calc
$^{33}\text{S}_a$	30.4	28.4	15.2	16.0
$^{33}\text{S}_b$	14.7	14.2	6.7	8.0
$^{33}\text{S}_{ab}$	9.5	9.7	1.7	1.8
$^{33}\text{S}_{aba}$	0.9	1.7	...	0.1

in a pure 3s orbital³ and 59 G for 2B in a pure 3p orbital²¹
 $[2B = 4/5\gamma_e\gamma_n\langle r^{-3} \rangle_{3p}]$ one may calculate that

$$c_1^2 = 0.533$$

and

$$c_2^2 = 0.55. \quad (17)$$

Using the hyperfine data of Schneider et al, one obtains $c_1^2 = 0.65$ and $c_2^2 = 0.44$. These results indicate that the electron is completely localized on the S_3^- ion. In addition it appears that the spin density on the central atom is less for S_3^- on MgO than in KCl. Schlick²⁸ has reported values

of $c_1^2 = 0.473$ and $c_2^2 = 0.528$ for O_3^- in $KClO_3$. A Hückle molecular orbital treatment yields $c_1^2 = c_2^2 = 0.5$.

In view of the lack of motion for ions such as CO_2^- , SO_2^- , and O_3^- on MgO it is a bit surprising that S_3^- is librating at 77°K. On the other hand, the larger size of the S_3^- ion may prevent it from fitting into a more restricted position such as an oxide ion vacancy. Schneider et al. observed motional averaging of SO_2^- and SeO_2^- in KCl and KBr at room temperature. This phenomenon was explained by the hopping of the paramagnetic molecule among its twelve equivalent equilibrium sites in the cubic crystal. Studies on the hindered motion of NO_2 in zeolites have demonstrated that libration of 45° from an equilibrium position (90° total angle) is sufficient to completely average any anisotropy. Such motion in the xy plane of the molecule is reasonable if the S_3^- ions are located on the edges or corners of the MgO crystallites, which are approximately 100 Å on a side. At room temperature it appears that the ions are also experiencing motion in the xz and yz planes.

The origin of the reducing electron is uncertain, although there is ample evidence that such electrons are available on the surface of MgO. Curiously, higher purity MgO has a greater capacity for reducing O_2 to O_2^- ; ²⁹ therefore, it is unlikely that impurity ions are directly involved. It has been argued that the electron transfer takes place at corner oxide ions, where there is maximum instability. ³⁰

The formation of S_3^- on the partially hydroxylated MgO may involve more than a simple electron transfer step. The simultaneous formation of S_3^- , the loss of the sulfur polymer,

and the formation of H_2S at 400°C suggest that a reaction such as



may occur. The absence of any paramagnetic S_n or S_{n-9} following the reaction at 400°C is evidence that the sulfur either completely reacts or that it desorbs. Actually, very weak hyperfine lines due to S_3 were observed at temperatures as low as 200°C ; however, at these temperatures the spectrum was strongly dominated by the S_n radical.

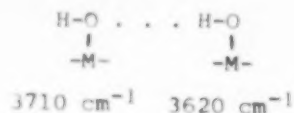
INFRARED STUDY OF SO_2 ON MAGNESIUM OXIDE

The Hydroxyl Band Spectrum of MgO

Imelik and coworkers³¹ reported that physisorbed water was desorbed from MgO at 150° under dynamic vacuum. This treatment also eliminated the 1640 cm^{-1} deformation band of water. Therefore, the bands in the $1100\text{--}1700\text{ cm}^{-1}$ region reported in Figure 13 can not be ascribed to water. We rather believe that they are due to carbonate species on the surface. The frequencies fall in the same range as those reported in the literature for carbonate species.³²

Anderson³³ observed bands at 3750 , 3710 and 3620 cm^{-1} which are ascribed to three types of OH groups on the MgO surface. The 3750 cm^{-1} band is attributed to isolated OH groups pointing out of the surface; whereas, the 3620 cm^{-1} band is assigned to OH groups with their oxygen linked to two Mg ions. The band at 3710 cm^{-1} only appeared after rehydration of MgO and is ascribed to an intermediate product between MgO and $\text{Mg}(\text{OH})_2$. Lisachenko et al.³⁴ disagree with

this interpretation of the 3620 and 3710 cm^{-1} bands. They interpret the 3620 cm^{-1} band as due to hydrogen bonded hydroxyl groups and the 3710 cm^{-1} band as due to hydroxyl groups with a free proton but with their oxygen hydrogen bonded to a neighboring OH group:



After heating at 300° we reported three additional bands at 3660, 3530, and 3390 cm^{-1} . These may be ascribed to preferred geometric arrangements for other hydrogen bonded OH groups. We agree with previous investigators^{33,34} concerning the assignment of the 3750 cm^{-1} band to isolated hydroxyl groups. However, as indicated in Figure 13, the 3710 cm^{-1} band, which occurs at 3725 cm^{-1} in our case, is already present during the initial dehydration process in contradiction with Anderson's work. Moreover, our adsorption data with SO_2 revealed that a similar band (3730 cm^{-1}) is present after adsorption. This suggests that the band is due to OH groups in the bulk MgO or that they are screened off from the SO_2 molecules by inaccessible pores.

From our data it is impossible to decide whether Anderson's interpretation or Lisachenko's is correct concerning the 3620 cm^{-1} OH groups. The broadness of the bands and the fact that these OH groups are more easily dehydrated than the 3750 cm^{-1} OH groups are experimental results in favor of Lisachenko's interpretation.

The Species Formed during the Adsorption and Desorption of SO₂ under Vacuum

No SO₂ bands around 1360 cm⁻¹ and 1150 cm⁻¹ are left in the spectrum after degassing the excess SO₂ at room temperature; hence, no physisorbed SO₂ remains on the surface. At the same time the 3740-3750 cm⁻¹ OH band does not reappear. To restore this 3750 cm⁻¹ band it is necessary to heat the sample to 300°.

The complex OH band spectrum of Figure 14a and b contains the 3725-3730 cm⁻¹ band, attributed to inaccessible OH groups, and three bands around 3670, 3600 and 3400 cm⁻¹. The latter can only come from the original 3750 cm⁻¹ band. The shifts to three lower frequencies could indicate three different strengths of interaction with only one sulfur species adsorbed on three different sites. It is, however, more probable that three different sulfur species are present on the surface. Each of them interacts with OH groups. This results in three different frequency shifts according to the type and strength of interaction in each individual case.

The broad band between 800-1100 cm⁻¹ (Figure 14a and b) does not allow an identification of the possible sulfur species on the surface at low temperatures. It is possible that SO₂ is present in the form of a strongly complexed surface species. In sulfinato complexes, where SO₂ is linked with one oxygen or both oxygens to the complexing ion, the free S-O stretching vibration absorbs in the range 1100-1050 cm⁻¹ while the ν_{as} (S-O-M) vibration adsorbs at still lower wave numbers. The

difference between the two frequencies is 100-200 cm^{-1} for sulfinato, O-complexes and 10-80 cm^{-1} for sulfinato O, O'-complexes³⁵. These frequencies fall in the broad adsorption range of 800-1100 cm^{-1} , but the existence of such complexed SO_2 cannot be verified from our experiments.

At 300° the 3750 cm^{-1} band is completely restored, which indicates that no OH groups remain hydrogen bonded or react with the sulfur species. At the same time the broad 800-1100 cm^{-1} absorption goes over to the five-band spectrum shown in Figure 14c. The most reasonable explanation is that certain surface species of SO_2 are desorbed and others react with the MgO surface.

The spectrum of Figure 14c agrees qualitatively with that of MgO doped with MgSO_3 (Figure 16b). In the latter spectrum bands occur also at 1220 and 1265 cm^{-1} which are not present in the degassed MgO samples of Figure 14c. The origin of these bands is not known. In the 800-1100 cm^{-1} region the free SO_3^{2-} has a nondegenerate vibration ν_1 at 961 cm^{-1} and a doubly degenerate vibration ν_3 at 1010 cm^{-1} ³⁶. If the C_{3v} symmetry is lowered to C_s the 1010 cm^{-1} band splits into two bands. Splitting of the degenerate ν_3 vibration of SO_3 occurs into sulfito complexes^{37,38}. If the SO_3^{2-} ion is bonded with its S atom to the surface the C_{3v} symmetry is preserved. If bonding occurs through O the symmetry can be lowered to C_s for unidentate complexes while it is always C_s in bidentate complexes. Furthermore, coordination through sulfur shifts the SO stretching bands to higher frequencies, whereas coordination through oxygen shifts them to lower frequencies relative to the frequencies

of the free ion³⁶.

In sulfito bidentate complexes Baldwin observed the ν_1 at 988 cm^{-1} and the two bands of ν_3 in the regions $1093\text{--}1070\text{ cm}^{-1}$ and $1036\text{--}1042\text{ cm}^{-1}$. These frequencies agree reasonably well with the 975 cm^{-1} , 1040 and 1070 cm^{-1} bands observed in our spectra (Figure 14c). This observation together with the similarity to the spectrum of MgSO_3 doped MgO is strong evidence for the existence of a SO_3^{2-} surface species on MgO . We believe also that the pair of bands at 925 cm^{-1} and 895 cm^{-1} belongs to the nearly degenerate ν_3 (E) vibration of a second SO_3^{2-} species. The latter species is less stable than the former as can be seen from Figure 14d. Following this reasoning the $1040\text{--}1070\text{ cm}^{-1}$ pair of bands is assigned to a SO_3^{2-} species coordinated through its sulfur while the $925\text{--}895\text{ cm}^{-1}$ pair of bands is assigned to a SO_3^{2-} species coordinated through an oxygen atom.

Also some samples have a weak 955 cm^{-1} band which completely disappears at 500° . The origin of this unstable band is unknown.

The 800° pretreated MgO has only weak SO_3^{2-} bands at the same frequencies as those shown in Figure 14c. This indicates the presence of very small amounts of SO_3^{2-} . One reason for this decrease is the loss in surface area due to the 800° pretreatment with respect to the 500° pretreatment. It also appears that the SO_3^{2-} may react to form other species since sulfite salts are unstable above 500° . The spectra of the SO_2 adsorbed on MgO pretreated at 800° predominantly show the features of the spectrum of SO_2 on MgO pretreated

at 500° and subsequently degassed at 800°, i.e., two broad bands at 1070 and 1020 cm^{-1} with a peak around 860 cm^{-1} . The most reasonable explanation for these bands is the formation of some SO_4 species. Blyholder and Cagle⁸ also give three frequencies at 865, 955 and 1055 cm^{-1} for a surface SO_4 species on Fe. Our frequencies on MgO fall in approximately the same range. A comparison of these frequencies with those of sulfato complexes indicates that a monodentate complex is probably formed on the surface³⁶.

A comparison of the spectra of SO_2 adsorbed on MgO and CaO reveals significant differences, although the overall reactions are similar. At low coverages it appears that SO_2 reacts with CaO at 25° to form a pyramidal sulfite¹⁰. This assignment by Low and coworkers is based on the observation of bands at 973, 925, and 632 cm^{-1} . The bands at 973 and 927 cm^{-1} are in agreement with two of those observed for SO_3^{2-} (A) on MgO. The rather complex spectrum obtained by degassing the CaO- SO_2 sample to 500° has been attributed to a surface sulfate; whereas, we attribute a somewhat similar spectrum to the formation of two sulfite species. Following treatment of the samples at 750-800° a much more complex spectrum was observed on CaO than on MgO. The resulting spectra were assigned to species such as $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_5^{2-}$, $\text{S}_3\text{O}_8^{2-}$, etc., for CaO and SO_4^{2-} for MgO.

Reaction of Adsorbed SO_2 with O_2

It is apparent from the spectra of Figure 15 that the sulfite groups on MgO react with oxygen to form new surface species. At least eleven bands are apparent in the spectrum of Figure 15c and other weak bands may be hidden beneath the

dominant ones. As the temperature is raised to 600 and 800° some of the bands diminish while new bands appear. Although the situation is complex, one may make reasonable assignments concerning the origin of the bands.

The oxidation products are probably sulfato complexes. The free sulfate ion has T_d symmetry. Its ν_3 and ν_4 vibrations are infrared active at 1105 and 613 cm^{-1} , respectively³⁶. When the ion is bonded through one oxygen the forbidden ν_1 vibration is allowed at 970 cm^{-1} and the triply degenerate ν_3 vibration splits into two bands. For a bidentate complex where SO_4^{2-} is bonded with two oxygens, the symmetry becomes C_{2v} with three bands from the split ν_3 vibration in addition to the one band from the ν_1 vibration. Two types of bidentate complexes are possible one is a chelating complex and the other is a bridging complex. Typically the ν_3 vibrational frequencies of the chelating complex (1230, 1120, 1060, and 960 cm^{-1}) are higher than those of the bridging complex (1160, 1100, 1030 and 970 cm^{-1})³⁶.

As indicated in Table 5c, the bands observed following reaction of the sulfite complex with oxygen at 400, 600 and 800° may be divided into three chelating and one bridging complex. Since the thermal treatment at 800° produces a drastic modification of the surface, it is not surprising that the surface complexes are different at 800° compared to 400°. A bridging complex and a sulfato complex denoted by C_1 were the first to decrease and a new complex appeared following reaction at 600°. The spectrum of a second chelating complex, C_2 , was also weaker at this

temperature. Such concomitant behavior of certain bands was used to make the assignments. At 600° a new chelating complex, C₃, appeared which was the dominant species following reaction at 800°.

At all three reaction temperatures bands appeared in the 1345-1390 cm⁻¹ region with a possible counterpart in the 1050-1060 cm⁻¹ region. Free SO₃ exhibits bands at 1391 and 1068 cm⁻¹; hence, it is reasonable to assume that the similar bands on MgO are due to strongly adsorbed SO₃ which is in equilibrium with the sulfato complexes. The hydroxyl bands at 3640 and 3430 cm⁻¹ may be shifted and the OH⁻ groups stabilized by interactions with the strongly bonded SO₃. The assignment of the bands to SO₃ is supported by the observation that the 1360 and 1390 cm⁻¹ bands did not appear on MgO pretreated at 800°, and the counterpart of the SO₃ spectrum at 1050 cm⁻¹ became less important than the pair of bands at 1170 and 1220 cm⁻¹. Pretreatment at 800° must destroy the sites responsible for the formation of the SO₃ species.

Low and coworkers¹⁰ likewise studied the reaction of adsorbed sulfur species with oxygen at elevated temperatures. They observed that the sulfate band pattern produced by degassing the sample at 750° became more like that of an ionic sulfate upon reaction with oxygen. They concluded that small patches or microcrystals of CaCO₃ are formed on the CaO surface. The spectrum of Figure 16c is probably due, in part, to the formation of corresponding microcrystals on MgO. A comparison of this spectrum with those of Figure 15 C-E shows that similarities exist; however, the presence of distinctly different bands indicates that more than one type of sulfate species is formed upon reaction with oxygen.

SECTION VII

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SECTION VIII

LIST OF PUBLICATIONS

1. "An Electron Paramagnetic Resonance Study of SO_2^- on Magnesium Oxide", R. A. Schoonheydt and J. H. Lunsford, J. Phys. Chem., 76, 323-328 (1972).
2. "Infrared Spectroscopic Investigation of the Adsorption and Reactions of SO_2 on MgO ", R. A. Schoonheydt and J. H. Lunsford, J. Catal., 26, 261-265 (1972).
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SECTION IX

GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

A_{iso}	isotropic hyperfine splitting.
$a_{ }, A_{ }$	hyperfine coupling parallel to a symmetry axis.
$a_{\perp}, A_{\perp}$	hyperfine coupling perpendicular to a symmetry axis.
a_{xx}, a_{yy}, a_{zz}	hyperfine coupling along the x, y, and z direction, respectively.
$b_{1,2,\dots}$	coefficient of an atomic orbital.
$c_{1,2,\dots}$	coefficient of an atomic orbital.
c_{2v}, c_s	symmetry notation for molecules.
$(1e), (5a_1)\dots$	sequence of molecular orbitals.
E	energy of a molecular orbital.
g	g factor.
$g_{ }$	g component for the magnetic field parallel to the axis of symmetry.
$g_{\perp}$	g component for the magnetic field perpendicular to the axis of symmetry.
g_{xx}, g_{yy}, g_{zz}	g component for the magnetic field along the x, y, and z direction, respectively.
G	gauss.

p_x, p_y, p_z	atomic wave functions with unit orbital angular momentum.
Q-band	30-35 GHz microwave region.
r	radius.
s	atomic wave function with zero orbital angular momentum.
X-band	9-10 GHz microwave region.
$2B$	anisotropic hyperfine coupling.
γ_e	magnetogyric ratio of the electron.
γ_n	magnetogyric ratio of the nucleus.
$\nu_{1,2,\dots}$	vibrational frequencies.
ϕ	bond angle.
ψ	wave function.

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16. ABSTRACT The purpose of the research reported here was to determine the structure and reactivity of adsorbed oxides of sulfur and other small sulfur-containing molecules. The molecules that were studied include the anion radicals of sulfur dioxide, sulfur trioxide, a triatomic sulfur species and carbonyl sulfide. Diamagnetic sulfite and sulfate ions, as well as covalently bonded oxides of sulfur, were also studied. The adsorbent was a high surface area magnesium oxide powder. Electron paramagnetic resonance and infrared spectroscopy were used to characterize the surface species. The results show that electronegative molecules such as sulfur dioxide adsorb either by an electron transfer from the solid, forming a negative radical ion, or by reacting with the oxide ions of the lattice. At room temperature the adsorbed sulfur dioxide anion radical may be oxidized with molecular oxygen to the sulfur trioxide anion radical; whereas, at elevated temperatures the sulfite ions may be oxidized. In contrast, the anion radical of carbonyl sulfide is very unstable and dissociates, presumably to elemental sulfur and carbon monoxide, at low temperatures. Elemental sulfur reacts with partially hydroxylated magnesium oxide, forming the triatomic negative ion, hydrogen sulfide, and other unidentified products.		
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a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Sulfur Compounds: Sulfur dioxide, Sulfur trioxide, Sulfate, Sulfides, Sulfite; Magnesium oxide; Spectrometry: Infrared; Electron paramagnetic resonance; Catalysis; Surface properties; Chemical reactions: Reduction, Oxidation.		
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